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# TECHNICAL THERMODYNAMICS

BY  
DR. GUSTAV ZEUNER

FIRST ENGLISH EDITION

FROM THE FIFTH COMPLETE AND REVISED EDITION OF  
"GRUNDZÜGE DER MECHANISCHEN WÄRMETHEORIE"

VOLUME I  
FUNDAMENTAL LAWS OF THERMODYNAMICS  
THEORY OF GASES

AUTHORIZED TRANSLATION BY

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*Professor of Mechanical Engineering, Lehigh University*



NEW YORK  
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## PREFACE.

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THE first edition of the present book appeared in 1859 under the title "Grundzüge der mechanischen Wärmetheorie" (Main Features of the Mechanical Theory of Heat).

This small publication of only twelve printer's forms (signatures) had for its purpose a clear and connected presentation of the results of the scattered work of different authors which had appeared up to that time, and also of the outcome of my own investigations which dealt particularly with the behavior of vapors; another object was to direct the attention of mechanical engineers to the great importance which the new theory of heat might assume in the further development of the theory of machines.

Under the same title there appeared in 1866 a revised and considerably enlarged second edition of the book; it was intended mainly for technical men, although the general theoretical portion was given more fully than was necessary, as an introduction to the study of the here pertinent technical problems.

This edition was translated into French by Maurice Arnthal and Achille Cazin under the title "Théorie mécanique de la Chaleur," Paris, Gauthier-Villars, 1869; Hirn had already reproduced in translation the first edition of my book in a special section of his work, "Exposition analytique et expérimentale de la Théorie mécanique de la Chaleur," Paris, 1862.

After the German edition was exhausted and for several years completely out of print, I resolved at the solicitation of the publishers to issue in 1877 a reprint of the second edition, because other obligations assumed by me rendered it impossible to prepare a revised, third edition; to this reprint I added, as



an appendix, a paper which I published in the "Zeitschrift des Vereins deutscher Ingenieure," Vol. 11, 1866, under the title "Theorie der überhitzten Wasserdämpfe"; a few omissions were made, but nothing else was changed in the arrangement and presentation of the whole material.

When reworking the third edition of the "Grundzüge der mechanischen Wärmetheorie" I had to completely give up the idea of simply revising the preceding editions and merely adding the necessary supplements. I then chose the title "Technical Thermodynamics" in order to bring out the fact that a wholly new treatise existed, and to emphasize strongly the new purpose which I had in view. In recent years there has appeared in the modern languages a whole series of works on Thermodynamics, some of them excellent and most of them written by physicists; the progress made by this comparatively young branch of Physics was certainly very considerable, but a keener glance at the results of these investigations also showed that scientific technology had reaped the main, and indeed we may say the greater, advantage from these results. This may be due in large measure to the fact that in the original development and further prosecution of Thermodynamics a prominent part was taken by engineers and the representatives of the engineering sciences—it is only necessary to mention the names of Carnot, Clapeyron, Rankine, Hirn, and Grashof. To collect the new technical acquisitions in the Thermodynamic dominion seemed to me the most important task of this revision.

There was also a special reason for distinguishing between the physical and technical treatment of Thermodynamics, and this was the need of the higher technical institutions of learning. The introduction into the curriculum of certain parts of technical mechanics and of the theory of machines demands at the technical high schools a different treatment for Thermodynamics than it can receive in the handbooks of physics and in the lectures on general physics. The arrangement and choice of material in the new book (accompanied by the use of the technical terminology and the peculiar graphical representation with which the young engineer must early become familiar) correspond in general to

the presentation which I have found suitable and fruitful, in my "Lectures on Thermodynamics as an Introduction to the Theory of Engines," during many years of activity as a teacher.

The wealth of the worked-up material and the desire to make the book a handy one seem to require the division of the work into two volumes; the first volume covers the Fundamental Laws of Thermodynamics and the Theory of Gases, whereas the second volume treats of the theory of vapors. While the second volume in its special technical application naturally devotes itself largely to the theory of steam engines and of refrigerating machines, the first volume gives a thorough discussion of hot- and cold-air engines, and of internal-combustion motors the principal representative of which at the present day is the gas engine.

In working up the fourth edition of the present book (1901) I did not expect to be again put in the position of undertaking another revision, for the book has been widely used during a long series of years and is particularly well known in technical circles.

Nevertheless when the publisher after a comparatively short period again approached me with the request to prepare a new edition I could not decline his proposition; to be sure I had to overcome many doubts and scruples, for now I hardly feel equal to the task.

In the long series of years of its existence, since the introduction of Thermodynamics into technical investigations, my book has pursued the aim of giving a bird's-eye view of all the work belonging to this field up to recent times; it therefore appears as a sort of review of the historical development of "Technical Thermodynamics," and to this is probably mainly due its favorable reception in technical circles.

I have clung to this point of view, it might possibly be called the standpoint of *Regnault's* experiments, in this new revision and therefore felt less obliged to lay stress on the recent observations—highly of course as I appreciate their value for current technical problems—because their theoretical discussion is amply provided for by the newer literary productions.

DR. GUSTAV ZEUNER.

DRESDEN, End of June 1905.

By the same author have appeared:

- Abhandlungen aus der mathematischen Statistik.** (Papers in Mathematical Statistics.) With 27 woodcuts and several tables. 8°. 1869. viii+220 pages. Mk. 6.
- Das Locomotiven-Blasrohr.** (The Locomotive Blast-pipe.) Experimental and theoretical investigations on the production of draft by steam jets and on the suction action of liquid jets in general. With 25 woodcuts and 2 lithographed tables. 8°. 1863. viii+231 pages. Mk. 5.
- Die Schiebersteuerungen.** (Valve Gears.) With special consideration of Locomotive Valve Gears. Sixth Edition. With 62 woodcuts printed in the text and 6 lithographed tables. 8°. xvi+259 pages. 1904. Paper, Mk. 8; bound, Mk. 9.
- Vorlesungen über Theorie der Turbine.** (Lectures on the Theory of Turbines.) With preparatory investigations in Technical Hydraulics. With 80 woodcuts printed in the text. 8°. xii+372 pages. 1899. Paper, Mk. 10; bound, Mk. 12.



## TRANSLATOR'S PREFACE.

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THIS treatise has maintained its leadership with the German technical public for forty years. It has molded their thought concerning engineering Thermodynamics and has given analytical expression to it. Dr. Zeuner was quick to see the necessity of taking this subject out of the department of Mathematical Physics, of casting it into simpler form, of bringing it within the range of engineers and technical students, and of limiting it to their interests. It will be found that his presentation combines German thoroughness with French elegance and simplicity.

In the Fifth German Edition (just completed) the distinguished author has brought the whole subject well up to date. He has given an adequate and conservative presentation of the subject of variable specific heats in gases and vapors; has subjected the whole question of the characteristic equation of superheated steam to careful revision and tested it by Battelli's experiments; has established more practical and satisfactory standards of comparison in steam engineering, has given us the kernels of the subject of refrigerating machinery and has gone fully into problems that the rapidly growing subject of gas engineering now submits for solution to the technical world.

The general plan of the work is to establish a few fundamental equations and deduce all results from these. The author has the engineer's instinct to check everything by experiment, and he also has an engineer's appreciation of the limitations imposed by practical conditions. The great clearness and simplicity per-

vading the whole presentation is largely due to Dr. Zeuner's own active and fruitful participation in the discussion and experiments connected with the great questions of steam and gas engineering as they arose. This participation developed in him a sound sense of proportion which enables him to here maintain the proper relations between theory, experiment, and construction.

It is no small achievement to have brought this advanced scientific subject within the reach and comprehension of that wide circle of efficient engineers who have only a moderate mathematical equipment. The author's constant reference to original sources, his frequent appeal to experiment, his many practical examples with real engineering data, and his convenient and far-reaching formulas and tables have always been highly appreciated by both the student and the practitioner of engineering. The independence of the several parts of the book, the simplicity and elegance of its mathematical presentation, its restriction to technical interests, render this book particularly suitable for study in engineering schools.

This English edition has had the benefit of the revision furnished by classroom work, for advance sheets of most of the treatise were supplied to, and studied with profit by, the Senior class in mechanical engineering at Lehigh University.

J. F. K.

BETHLEHEM, PA., January, 1907.

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# TECHNICAL THERMODYNAMICS.

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## INTRODUCTION.

WHEN the second edition of this book appeared nearly forty years ago under its earliest title, "Grundzüge der mechanischen Wärmetheorie" (Main Features of the Mechanical Theory of Heat), Leipsic, 1866, it was prefaced by an Introduction the purpose of which was to present the general, physical, foundations of the Theory of Heat.

This Introduction started with the Elastic-solid Theory of Light for the purpose of showing that it is necessary to imagine the particles of the body in motion to explain the simplest heat phenomena, particularly heating by radiation.

"The investigations of the properties of light"—thus the Introduction began at that time—"have led to the generally prevailing view that the whole universe is filled with a fine and elastic substance, ether; a substance which permeates all bodies and whose particles are in vibrating, oscillating, motion.

"Just as an oscillating body sets the surrounding air into oscillations which spread themselves wavelike in all directions and, reaching the ear, generate under certain circumstances the sensation of sound, so, according to the aforesaid undulatory theory, there proceed from an illuminating body oscillations of the ether which, entering the eye under certain conditions, produce the impression of light.

"In the one case the particles of air oscillate, in the other case the particles of ether oscillate about their positions of equilibrium, and the propagation of the sound or of the light consists in start-

ing, from the center of the disturbance, oscillations in every direction, so that constantly new particles are set into vibration by the action of the preceding ones.

“The difference of tones in acoustic motion is due to the greater or less number of vibrations executed by the particles of air in a certain time, say in a second; the quicker the oscillations follow one another, the higher the tone; the velocity of propagation is independent of the duration of an oscillation.

“In like manner difference of color is explained by difference in the number of ether vibrations in a certain time; here also the velocity, with which the waves of the differently colored rays of light are propagated in space, is the same for all rays.

“The hypothesis that light is no substance but something analogous to sound, that it consists in the propagation of the oscillatory motion of the smallest parts of a peculiar medium (Undulatory Theory), was first suggested by Huyghens (1690), but not till the beginning of the century, till it was shown (by the work of Young and Fresnel, and by the mathematical investigations of Cauchy, Green, and others) that by means of this hypothesis there could be explained clearly and simply all the phenomena of light, diffraction, polarization, interference and double refraction, was the Undulatory Theory generally accepted, and the Emission Theory set up by Newton rejected, the latter theory representing light as a substance whose particles were emitted with great velocity by illuminating bodies.

“The general acceptance of the undulatory theory, for the explanation of the phenomena of light, has caused the imponderables to be generally banished from physics; the view spreads more and more that light and heat, electricity and magnetism, depend upon the motions of the smallest parts of one and the same substance, ether.

“The acceptance of the undulatory theory for light immediately led to the inference that radiant heat must be a motion of smallest particles.

“It is an undoubted consequence of the beautiful experiments of Melloni that radiant heat like light consists in the transverse oscillations of the ether permeating all bodies.

“Heat rays are nothing but invisible rays of light (which consist of vibrations of the ether), whose time of oscillation is different from that of the visible rays.

“The eye can no longer detect such rays as light, just as the ear is incapable of hearing certain tones, in other words, incapable of recognizing vibrations of the air whose time of oscillation falls below a certain value.

“If through a small aperture in a window-shutter of a dark room we allow rays of the sun to pass through a glass prism, there will appear, as is well known, on an opposite white screen a picture of colored stripes; they are the rainbow colors arranged in the order: red, orange, yellow, green, light blue, dark blue, and violet. The white sunlight thus shows itself to be composed of different colored rays which can be thus separated by virtue of their difference in refracting power; they cannot be decomposed any further, and when recombined will again produce white light.

“Red is deflected the least and violet the most; the difference of deflection stands in a direct relation to the wave lengths of the different colored rays and to the number of vibrations which the ether particles make in a certain time. According to Fresnel, at the extreme red of the spectrum this number of vibrations is 487 billions, and at the extreme violet the number is 764 billions.

“The spread of the colors is different in the spectrum; it is greatest in the violet and least in the yellow; on the other hand, the strength of the light is least in the violet, increases up to the yellow, and then again diminishes toward the red. In the yellow, therefore, the light is of maximum strength.

“Now a further investigation of the spectrum results in something of special importance for our discussion: the area upon which the spectrum falls is warmed, but this warming has a distribution that is different from that of the strength of the light.

“If we develop the spectrum by a prism of rock salt, because this most completely permits the heat rays to pass through, then the heating will be least at the violet end, will increase gradually toward the red end of the spectrum, but will not reach its maxi-

mum until it has passed into the dark space beyond the red, where it again diminishes.

"The heating can be detected over two thirds of the visible spectrum and also beyond the red, that is, at the less refrangible end. The heat spectrum therefore falls partly on the optical spectrum and partly on the dark space beyond the red.

"From this we must conclude that besides the visible rays, the rays of light proper, there are other rays which we do not see that make themselves known by heating. These rays, constituting the heat spectrum, are less refrangible, have greater wave length and a greater time of oscillation. The greatest heating therefore occurs with those rays in which the ether particles make less than 481 billions of vibrations per second.

"For the sake of completeness we may add that investigation of the other end of the spectrum has led to no less interesting results.

"Rays in which the number of ether vibrations exceed 764 billions per second also escape the eye, but they nevertheless do exist and express themselves principally by the chemical changes which they produce in certain bodies.

"Photography depends on the ability of rays of light to decompose certain chemical combinations; a closer investigation of the spectrum shows that the red possesses this power to the least degree and the violet to the greatest degree, but that the greatest chemical action obtains with the invisible rays lying beyond the violet, the so-called ultra-violet rays.

"The presence of the ultra-violet rays manifests itself, moreover, by fluorescence. For example, certain colored plant-extracts glow when they are brought into the dark space beyond the violet, which is explained by the assumption that these bodies are capable of reducing the number of vibrations of the ultra-violet rays impinging upon them, and thus send forth visible rays.

"On account of these properties of the spectrum near the violet end, this portion has been called the chemical or fluorescence spectrum.

"From what has been said it appears that the visible spectrum is only a part of the larger one, and indeed the smaller part.

"The visible series of colors has often been compared with a



musical scale in which each color-tone can be determined on the basis of the known number of vibrations of the different colors; this acoustic division shows that the visible spectrum does not quite occupy an octave, but that, so far as we now know, the whole spectrum occupies four octaves.

"The greater part of it falls on the heat spectrum, and the heat rays possess properties like those of the light rays; it has been shown that they, too, exhibit the phenomenon of refraction and of interference, which phenomena can only be explained by ether vibrations; the experiments on polarization and double refraction of the heat rays likewise show that here, as with rays of light, we have to do with the transverse vibrations of the ether.

"Consequently if we wish to embrace the ether vibration by one name, that name must be *Heat*.

"A body which is capable of setting the surrounding ether into oscillation, and this property belongs to all bodies, sends out different kinds of rays, and among these there is a certain kind which affects our nerves of feeling and exerts a warming effect in the ordinary sense. Another kind of these rays, for which the number of vibrations falls between the just designated limits, can, in addition, produce in our eyes the sensation of light. Still other rays, and in general such as possess a still greater number of vibrations than the 'illuminating' rays, announce their presence by their chemical actions and by fluorescence.

"The results of the investigation of the spectrum which we have thus briefly emphasized, and according to which radiant heat doubtless consists in the propagation of oscillatory motion of the space-filling ether, lead at once to the very probable assumption that the heat contained in a body has its origin mainly in the oscillations of the smallest particles."

Connected with this Theory of Light, so generally accepted forty years ago, and with the atomic view of the constitution of bodies, there were then separately and partially developed certain hypotheses concerning the internal motion of bodies which were reported in the 1866 Introduction as follows:

"That view of the constitution of bodies is the most wide-spread which considers the body as made up of invariable particles, 'atoms,' whose distances apart are relatively very great; it is the view that was first definitely expressed by Ampère, Poisson, and Cauchy.

"The atoms are so small that a quantity of matter imperceptible to our senses may contain an uncommonly large number of them, and there are as many kinds as there are chemically simple elements.

"These atoms attract each other, and several of them, of the same or of different kinds, may combine to form a group, and such a group is called a molecule.

"In this way chemically compound bodies arise. The different grouping of like atoms also explains why (according to Clausius<sup>1</sup>) some bodies behave differently in a physical way, although chemically they may have the same composition.

"The relatively large spaces between the molecules are filled with ether. The ether atoms, which are very small in comparison to their mutual distances, and in comparison to the atoms of the body, act so as to repel each other, and so as to be attracted by the atoms of the body. In consequence of the action of these forces the ether surrounds the molecules and atoms in atmospheric fashion. These atmospheres, whose density diminishes from within outward, constitute with their kernel an individual whole. An atom with its envelope of ether Redtenbacher called a 'Dynamide,' while, according to his view, a union of atoms (molecule) with a common ether atmosphere is called a compound dynamide.<sup>2</sup>

"If we imagine heat rays to fall on a body, then the oscillating particles of ether will transfer their motion in part to the particles of this body, or to ether particles contained within the body, or to both of them simultaneously, and strengthen the motion already existing within the body.

"We then say that the body has been heated; it can, by contact

<sup>1</sup> Clausius, Über die Natur des Ozons. Poggendorff's Annalen, Vol. 103, p. 644.

<sup>2</sup> Redtenbacher, "Dynamidensystem." "Grundzüge einer mechanischen Physik." Mannheim, 1857.

with our nerves of feeling, produce the same sensation as the heat rays themselves.

"Conversely, motions within the interior of the body can be transferred to the surrounding ether; we can then say the body radiates heat.

"Only in one point do the views diverge, namely, as to the question whether the so-called heat motion is caused by the motion of the atoms, i.e., of the material parts of the body, or by the motion of the ether particles collected in the body.

"Redtenbacher (born July 25, 1809, died April 16, 1863) assumed that the heat motion consisted in the radial motion of the ether envelopes surrounding the atoms or molecules of the body; these envelopes contract and expand. When these envelopes are completely at rest the body is absolutely cold. If there is equilibrium between the attraction and repulsion of the individual dynamides, the body has an independent volume of its own. On the other hand, if the repulsion is in excess, the collection of dynamides must be enclosed by a solid envelope; this latter case corresponds to the gaseous condition; in the former case the body may exist in the solid or liquid state; in the fluid condition the dynamides are free to move relatively to one another without altering their relative distances and therefore without changing the total volume.

"Clausius<sup>1</sup> (born Jan. 2, 1822, died Aug. 24, 1888) defended another view with far-reaching consequences. According to him the heat motion consisted in the motion of the molecules, i.e., of the material parts of the bodies, this motion differing in solid, liquid, and gaseous bodies. In the solid condition the molecules move about certain positions of equilibrium, they oscillate, and indeed under the influence of forces which they mutually exert on one another. Besides the rectilinear oscillatory motions of the molecules there can also arise rotary oscillations about the center of gravity, and there may occur motions of the constituents, i.e., of the atoms of the molecule.

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<sup>1</sup> Clausius, Über die Art der Bewegung, welche wir Wärme nennen. Poggendorff's Annalen, Vol. 100, p. 353.—Clausius, Über das Wesen der Wärme, verglichen mit Licht und Schall. A popular address. Zurich, 1857.

"In the liquid condition there occurs an oscillating, rolling, and progressive motion; the kinetic energy of the motion, in comparison with the mutual attraction of the molecules, is not great enough to completely separate them from one another; even without an external pressure they keep themselves within a certain volume.

"In the gaseous condition the molecules have passed wholly beyond the spheres of their mutual attraction, they move rectilinearly in accordance with the law of inertia, obey the laws of elastic impact when they collide, and they rotate; it is probable that in gases there may simultaneously occur oscillating motions of the constituents, of the atoms in the molecules.

"That the principal properties of the gases can be explained by rectilinear progressive motions of the molecules was shown before Clausius by Krönig<sup>1</sup> through simple calculations; indeed the idea underlying the latter's calculations and in part those of Clausius goes much further back. Fuller details about this matter may be found in the writings of Le Sage."<sup>2</sup>

The Introduction of 1866 thus reported on definitely formulated hypotheses concerning heat motion, but even then the scientific development was such as to raise doubts as to the reliability and value of such hypothetical details. At that time the only certain view seemed to be that heat was motion of the particles, but the kind of motion was even then doubtful and, for the purposes of the mechanical theory of heat, a matter of indifference.

The Introduction of 1866 continues: "It would be of indisputable importance for the further cultivation of the mechanical theory of heat if the problem in question could be decided, and if the kind of heat motion in bodies were known.

<sup>1</sup>"Grundzüge einer Theorie der Gase." Poggendorff's Annalen, Vol. 99, p. 315.

<sup>2</sup>Deux traités de physique mécanique publiés par Pierre Prevost. Geneva and Paris, 1818. The first part contains the work of Le Sage, in which the view expressed about the constitution of gases is quite similar to that recently adopted, in accordance with the laws of the mechanical theory of heat. Le Sage mentions a series of writers (page 126) who had already expressed similar views; this was done with particular definiteness by Daniel Bernoulli.

"It is of great interest to compare the course of development of our Mechanical Theory of Light with the development of the Mechanical Theory of Heat or of Thermodynamics. }

"The Theory of Light starts at once with a perfectly determined mode of motion of the ether; it is assumed that the particles of ether describe paths about their positions of equilibrium under the action of a force of attraction which is directly proportional to the distance of the particle from the position of equilibrium, and this simple hypothesis concerning the nature of Light motion led to discoveries which we count among the most splendid in science.

"An essentially different path was pursued in the investigations on the theory of *Heat* after the view was given up that heat is a substance. Of the numerous works on this subject but few start with an assumption of a particular kind of heat motion, and these few investigations relate only to the behavior of gases.

"In general the mathematical developments avoided making definite assumptions concerning the nature of the motion which we call heat, and this we will also do in the further course of the present treatise.

"If we nevertheless here and there suggest the probable constitution of bodies and their condition of motion, it will only be for the purpose of rendering more easy the understanding and prosecution of the mathematical presentation.

"We may therefore say that the Mechanical Theory of Heat rests upon simpler laws than the Theory of Light, for in the latter we not only assume that light is a motion of the smallest parts of a substance, but simultaneously adopt a particular hypothesis in the investigations concerning the nature of this motion.

"In the newer theory of Heat the only assumption which is at first made is a very simple one, that the sensible heat of a body is a molecular motion. Heating or cooling a body consists in strengthening or weakening this motion. If the body is subjected to heat rays of a certain intensity, or if it is in contact with a body in which the motion is greater, then its own molecular motion may be strengthened, it is sensibly heated; cooling consists in giving off motion to the surrounding ether or to other bodies.

"The Kinetic Energy serves as a measure of the strength of the motion of a material particle of definite mass moving at a particular instant with a certain velocity; this energy is the work which is necessary to bring the mass from a condition of rest to this velocity, or it is the work which is produced when the mass passes from a condition of velocity to one of rest, regardless of the manner in which the velocity changes are effected.

"Now if we conceive of the body as a combination of material points (body and ether atoms) which act upon each other with certain forces, and which are engaged in any sort of oscillation and rotation, then there is stored at a certain instant in the whole system a definite amount of mechanical work, whatever the arrangement of the constituents and whatever the magnitude of the instantaneous velocity of every individual point may be.

"First of all, the total kinetic energy is a quantity that can be stated definitely and is the half-sum of all the products of the masses of the various material points each multiplied by the square of the instantaneous velocity of the point in question; consequently a strengthening or weakening of the molecular motion in a body consists in an increase or decrease of the sum of the energies of all the separate oscillating motions.

"If we (temporarily) designate this store of work in the body by the name 'vibration work,' then from all that has preceded we may at once conclude that the sensible heat in a body stands in a certain relation to this vibration work, and the thought nearest is that a sensible heating or cooling of a body consists precisely and only in the increase or decrease of the vibration work. But in saying this we do not at all mean to state that a supply of heat to a body must always have as a consequence an increase of the vibration work; even without the ordinary experiences the contrary may be expected.

"A system of connected material points (which act on each other by forces and are in oscillating motion) will experience changes in consequence of actions which it exerts on some other outside system, and this will be due not only to the change of vibration work, but in general also to the change in the relative distances of the middle positions of the



oscillating material points. Now whatever the forces may be which act or are overcome in changes of this sort, these changes will always consume work or they will produce work. The forces here mentioned are of two kinds; we have to distinguish between the forces (of attraction or repulsion) with which the material parts of the body themselves act on one another and those external forces, acting from the outside on the system, which are due to the actions of a second system upon the first. These external forces usually make themselves felt as pressures against the total outer surface of the body or against a part of it. Now the whole work, which in such a case is consumed or produced in consequence of the change in arrangement of the smallest parts of the body or system of material points, will hereafter be briefly called *disgregation work*.<sup>1</sup>

"We can now say that every change of condition of a body is connected with an expenditure or production of vibration work or of *disgregation work*, or of both simultaneously.

"If we consider more closely the changes which arise in a body that is receiving or rejecting heat, we will in general notice also changes of volume, usually accompanied by the overcoming of external forces (pressures). We conclude from this that the heat supplied to a body also, in general, effects a change in the arrangement of the constituents, and accordingly *disgregation work* is consumed or produced; without doubt in so doing the quality of heat stands in a certain relation to this work of *disgregation*. Since such a relation also exists with the simultaneously occurring change of vibration work, the question becomes imminent as to what relations probably exist between the magnitudes mentioned.

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<sup>1</sup> The word "*disgregation*" was first used by Clausius; he understood by this term the degree of division of a body, and when he indicated a change of arrangement of the smallest parts of a body, of the kind described above in the text, he spoke of "changes of *disgregation* of the body." See "Über die Anwendung des Satzes von der Äquivalenz der Verwandlungen auf die innere Arbeit." Poggendorff's *Annalen*, 1862, Vol. 116, p. 73. Also, Clausius, "*Abhandlungen über die mechanische Wärmetheorie*." Brunswick, 1864, *Abhandlung VI*.

"Now in this respect the mechanical theory of heat starts with the following assumption:

"The quantity of heat which is supplied to or withdrawn from a body is *directly proportional* to the sum of the simultaneously occurring changes in the vibration and disgregation work of the body.

"It is this hypothesis which underlies all our future investigations, and we must now more fully test its probability before we can utilize it as the basis of the mathematical development.

"According to the assumption made we can directly measure a certain quantity of heat by the work which it has performed, and therefore the above principle has also been simply enunciated in the words heat and work are equivalent. The absorption of heat on the part of a body appears to be synonymous with an absorption of work. Heat absorption consists in an increase, and heat rejection in a decrease, of the vibration and disgregation work of the body. If this assumption is correct, then we must immediately conclude that we can directly produce changes in a body by the performance of work (compression and so on) similar to those occasioned by a supply of heat; conversely, through the performance of work by the body (by its expansion and the overcoming of an external pressure) changes take place in its interior similar to those observed when the body radiates heat or gives it off by conduction to other bodies.

"We must furthermore conclude that the absorbed heat or work, which in general is expended to increase the vibration work (sensible heat) and to change the arrangement of the constituents, is solely expended in augmenting the vibration work (increasing the temperature) when the disgregation work is zero or infinitesimal.

"We must also accept the possibility that under certain conditions the sensible heat may remain unchanged, and that then the whole heat supplied to a body is consumed in changing the arrangement of the constituents."

Since these words were written, however, it is not only the kind of motion which constitutes heat that is in doubt, but whether what we feel to be heat is at all due to the motions of particles. The whole line of thought of the Introduction started with the Elastic-solid Theory of Light. But according to the electromagnetic theory it is not at all necessary to transmit motions, changes of position, energy from one body to another, but only electrical and magnetic changes.

And so to-day, more significantly even than forty years ago, it is true that the mechanical theory of heat can be founded on experience without entering into the question as to the nature of heat.

Therefore what at the present time seems to be really convincing and fundamental for the Mechanical Theory is the presentation, given in the Introduction of 1866:

It has long been known that a heating of bodies is always observed when there is friction between two bodies, when there is impact, and whenever work disappears during the interaction of two bodies or, as it is generally expressed, whenever losses of work take place; the accompanying heating may sometimes be very considerable.

Count Rumford<sup>1</sup> was the first to appreciate more clearly this well-known phenomenon, and to draw the conclusion that heat could be generated by mechanical work; he also tried to determine the relation between the work consumed and the heat quantity generated.

He compared the work consumed during the boring of the tube of a cannon with the degree of heating of the tube, which he ascertained from the rise in temperature of the water surrounding the tube. The experiment gave no decisive results because the losses of heat were not considered and because here evidently only a part of the work was expended in increasing the vibration work, the sensible heat, the rest being spent in disgregation work (separation of the metallic parts by drilling) which cannot be directly determined.

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<sup>1</sup> Phil. Trans., 1798. "An experimental Inquiry concerning the Source of the Heat which is excited by Friction."

Humphry Davy<sup>1</sup> adopted Rumford's view and sought to establish its correctness by other experiments. He showed that two pieces of ice rubbed against each other at 0° C. temperature, under the receiver of an air-pump, could be melted, and concluded that motion was the cause of the heat developed, which here showed itself by the melting of the ice.

The great distinction of first expressing in definite fashion the principle of the equivalence of heat and work belongs to the German Dr. J. R. Mayer of Heilbronn (born November 25, 1814, died March 20, 1878). His treatise "*Bemerkungen über die Kräfte der unbelebten Natur*,"<sup>2</sup> which appeared in 1842, contains upon a few pages the most interesting conclusions.

Mayer expressed himself with great clearness on the question; he showed that one could heat water in a vessel by shaking (performance of work), i.e., could raise the temperature of the water; he concluded that by performing work under high pressure (compression) ice could be transformed into water, which was later on confirmed by Mousson's experiments; and he expressly says at the end of his treatise: "We must find out how high a particular weight must be raised above the surface of the earth in order that its falling power may be equivalent to the heating of an equal weight of water from 0° to 1° C."

The height in question he then gives as 365 meters.

Mayer was therefore the first to definitely announce that the quantity of heat generated by the performance of work was proportional to the work consumed, and that the one could be directly measured by the other, while up to that time the idea had only been recognized and expressed that, in general, a certain relation between heat and work might exist.

First of all, the proportionality mentioned had to be established by reliable experiments, before one could pass to the mathematical treatment of the problem with prospect of success.

To measure quantities of heat the unit that must be taken is

<sup>1</sup> "Researches on Heat, Light, and Respiration," in Boddoe's *West Country Contributions*. Compare Joule, *Phil. Trans.* for 1842.

<sup>2</sup> *Annalen von Wöhler und Liebig*. May number, 1842.

that quantity of heat which will raise the unit of weight of water (1 kg) from  $0^{\circ}$  to  $1^{\circ}$  C. [or 1 lb. of water from  $32^{\circ}$  to  $33^{\circ}$  F.]. Now if heat and work are really equivalent, we can measure quantities of heat in the same way as work, only we must know how large a quantity of heat (in units of heat, in calories) [British thermal units] corresponds to the unit of work (1 mkg) [1 foot-pound] or how much work corresponds to a unit of heat.

This question was answered indubitably by the beautiful and manifold experiments of the Englishman Joule (born December 24, 1818, died October 11, 1889).

His experiments not only showed that heat could be generated by work, but also that the generated quantity of heat is always directly proportional to the work expended. The different experiments invariably led to almost the same relation, and indeed it appeared that the work of 424 mkg generated a quantity of heat exactly equivalent to the unit of heat, i.e., to a quantity of heat which could warm 1 kg of water from  $0^{\circ}$  to  $1^{\circ}$  C. [1 lb. of water from  $32^{\circ}$  to  $33^{\circ}$  F.].

The work value 424 mkg [772.83] is called "work equivalent of the unit of heat," or briefly "the mechanical equivalent of heat"; conversely, the quantity of heat which corresponds to the unit of work, 1 mkg [1 ft.-lb.], is called the "Thermal equivalent of the unit of work."

The value for the mechanical equivalent of heat found by Joule was confirmed later by other experiments.

To Joule therefore undoubtedly belongs the merit of having first reliably determined this important quantity; it is just as certain, however, that Mayer was the first to direct attention to the existence of this important constant. If Mayer, as the quotation from his paper shows, gave too small a value to this constant (he determined the value from observation on the heat released during the compression of a gas), then it was due solely to the fact that he had to introduce into his computations some quantities which were not at that time determined with sufficient accuracy.

The experiments for the determination of the value of the

mechanical equivalent of heat must be arranged and conducted with great care; it is a question of determining accurately the work which is completely expended in the generation of sensible heat and then to determine this quantity of heat itself.

It is only possible to do both if we choose such bodies, for the absorption of the generated heat, that the experiment can leave no permanent change in the arrangement of their constituents.

As was just mentioned, all the work must be utilized to increase the vibration work, i.e., the sensible heat; no part, or only an infinitesimal part, may here withdraw itself from direct observation as disgregation work.

Liquids, like water and mercury, are bodies which fulfill these conditions at low temperatures and small differences of temperature, and these were employed by Joule. To generate heat he, at the start, made use of the work which disappears with friction.

In one series of experiments<sup>1</sup> a vessel filled with mercury contained two cast-iron disks, one of them stationary and the other pressed against the first by a lever and set into rotation by falling weights. The magnitudes of the weights and the heights through which they fell gave, of course, after suitable corrections, the work which was expended in overcoming the friction. On the other hand the rise in temperature of the mercury and consideration of the heat lost by radiation enabled Joule to determine the quantity of heat generated by the friction.

The experiments were conducted under different conditions, but all gave the same relation between the work expended and the heat generated. The mean value of the mechanical equivalent of heat was thus found to be 425.18 mkg [775.01 ft-lb.].

In another series of experiments friction was generated between solid and liquid bodies.

In a vessel there was placed water or mercury and a stirring apparatus which was set in rotation by falling weights. In order to transfer the work more rapidly to the liquid and to convert it

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<sup>1</sup> Joule, Phil. Transactions for the year 1850, p. 1.

into heat, perforated partitions were placed in the vessel, the wings of the stirring-gear fitting these apertures quite closely.

These experiments led to the same result as the preceding ones. Joule found 423.92 mkg [772.71] for brass in water, and 424.68 mkg [774.10] for iron in mercury, and concluded from all his experiments that the probable value was 423.55 mkg [772.04 ft-lb.], in place of which we will hereafter use 424 [772.86].

In a subsequent experiment Joule compressed atmospheric air in a pump and forced it into a spherical vessel till the pressure rose to 22 atmospheres, while the vessel was immersed in a water calorimeter. From the rise in temperature of the water in the calorimeter the heat generated was determined; the work of compression transformed into heat was the work consumed in running the force-pump.

These experiments gave 437.77 mkg [797.96 ft-lb.] for the mechanical equivalent of heat; they are not as reliable as those already mentioned because the losses of work in the pump are difficult to ascertain, particularly the friction of the piston.

After Joule, an ingenious experiment was conducted by Hirn<sup>1</sup>; this experiment is of particular interest because Hirn transformed into heat the work which disappears during the impact of solid bodies, and because then some of the work expended was changed into disgregation work which Hirn cleverly knew how to determine.

Two heavy prismatic blocks, one of wood and the other of iron, were suspended pendulum fashion, so that their axes coincided when their ends touched. On the end of the wooden block, that toward the iron one, there was fastened an iron plate, against which a small lead cylinder could be placed.

The iron block was now lifted like a pendulum to a certain height and allowed to fall freely, so that in its lowest position it struck the lead cylinder and knocked the backing of the latter, the wooden block, up to a certain height.

In consequence of the impact the lead cylinder was compressed and heated. The heat generated was determined by filling, immediately after the impact, the hollow part of the lead

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<sup>1</sup> Hirn, *Théorie mécanique de la chaleur*, p. 58; 2d ed., Paris, 1865.



cylinder with a measured amount of water of known temperature, noting its rise in temperature and applying suitable corrections.

The energy contained in the iron block at the instant of impact was calculated directly from its weight and the height through which it fell. But this energy was by no means solely expended in the generation of heat; to determine the amount thus expended it is first necessary to ascertain how much was lost during impact, or rather how much energy remained in the blocks. For this purpose *Hirn* observed how high the iron block rebounded and how high the wooden block rose. From the weights and these lifts of the two blocks the work remaining in them was found, and then the work done on the lead cylinder and there transformed into heat could easily be ascertained.

In this way *Hirn* found the mechanical equivalent of heat to be 425 mkg [774.68 ft-lb.].

Therefore by all these experiments it is shown that through mechanical work the same phenomena can be produced in a body as by the supply of heat; hence the only question still to be raised is, whether a body giving off work by overcoming an external pressure during expansion also experiences those changes which take place with the loss of heat of the body by radiation or conduction, and whether the work performed by the body stands in the same relation to the diminution of the heat contained in the body.

Although this question may be immediately answered in the affirmative from all that has preceded, nevertheless we call attention to the fact that, in this particular also, observations exist.

First of all, we may point to the long-known fact that the temperature of a gas diminishes when it expands, doing work by the overcoming of pressure; heat therefore disappears, and the disappeared quantity of heat will bear to the work produced the definite ratio already given. Direct observations for this case do not exist, but the proof in question has been furnished for steam by *Hirn*.<sup>1</sup>

*Hirn* observed the quantity of water which was converted in

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<sup>1</sup> *Hirn*, "Recherches sur l'équivalent mécanique de la chaleur, présentées à la société de physique de Berlin." Paris, 1858.

a certain time into steam in the boiler of a large steam-engine and was then supplied to the steam-cylinder. As the pressure and temperature of this steam were both observed, the quantity of heat which it contained was known from Regnault's experiments. Steam, after leaving the cylinder, was condensed, and from the quantity and temperature of the injected water and of the condensed steam the quantity of heat was computed which the steam still possessed when it entered the condenser.

According to the mechanical theory of heat, and therefore according to the views developed above, the heat contained in the steam at its exit from the steam-cylinder must be "less" than the quantity of heat it contained at its entrance, and indeed the difference must correspond exactly to the work performed by the steam, which work was determined by experiments with the brake. Now Hirn not only observed such a difference, but Clausius<sup>1</sup> has also shown that the quantity of heat which disappeared in Hirn's steam-engine bears to the work performed the ratio demanded by theory.

In the different experiments there was performed, for every unit of heat, 399 to 427 mkg of work, and the mean of all the values obtained amounted to 413 mkg [752.76]; these results, therefore, a value approximately like that given by Joule.

The discrepancy is easily explained by the difficulties which must be overcome in experimenting on so grand a scale (the steam-engines developed over 100 horse-power); we must rather wonder at the cleverness with which the skillful experimenter conducted the experiments; the mechanical sciences are indebted to him also for the solution of other highly important problems.

If, finally, we collect the results of the experimental investigations adduced, we may well regard as proved the first law of Thermodynamics, "that heat and work are equivalent," i.e., we are justified, in the following investigations, in starting with the assumption: "Work can be obtained from heat and, conversely, heat can be generated by work; furthermore, that in so doing the consumed or generated unit of heat corresponds to a work

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<sup>1</sup> Hirn. *ibid.*, p. 134. (Report on the work in question to the physical society of Berlin by Prof. Dr. Clausius.)

of 424 mkg [772.83 ft-lb.], and, conversely, that a unit of work corresponds to  $\frac{1}{424} \left[ \frac{1}{772.83} \right]$  of a unit of heat, understanding by a unit of heat the quantity of heat which is necessary to raise one kilogram [pound] of water from 0° to 1° C. [32° to 33° F.].”

The more accurate determination of the mechanical equivalent of heat has repeatedly occupied experimenters during the last decades, and the reader is referred to the text-books on Physics for the methods of observation employed; but for technical investigations it is probably best for the present to stick to the mean value (424 mkg) [772.83 ft-lb.] given by Joule; following the practice of Clausius, this has been done throughout the present book.

## **FIRST SECTION**

# **Fundamental Equations of Thermodynamics**



## § 1. PRELIMINARY REMARKS.

The changes of state of a body which are connected with an absorption of heat, and which we can certainly regard as a consequence of such an absorption, will now be subjected to an investigation under the supposition that a condition of equilibrium exists, and that therefore neither the body as a whole nor its parts are undergoing visible changes of position connected with changes of velocity.

Moreover, it is assumed that while there are changes in the state of aggregation, there do not simultaneously occur chemical changes; consequently, according to the prevailing theory, there do not occur changes in the grouping of the atoms within their molecules.

Under these limiting assumptions, to which we will almost immediately add another, the state of the body is completely determined by its weight, its volume, and its pressure. Now, whether we are thinking of a body of finite extent or of the smallest part, we can refer, for the sake of simplicity, these determining magnitudes to the unit of weight of a body; for instance, only the volume referred to the unit of weight, or specific volume, will here be considered.

As specific pressure we designate the pressure in pounds acting upon the unit of area (kg per sq. meter) [lb. per sq. ft.], but here we introduce the additional limitation that the pressure is the same for all planes passing through the point in question; this is an assumption which at least always holds for liquid and gaseous bodies; furthermore, we assume that this pressure is the same at all parts of a body, and therefore is the

same at all parts of its surface; we now know fully the kind of body which will be the subject of the following investigation. A body of the described kind we will designate (in a wider sense than is customary) as homogeneous, or (following Grashof) as a body of uniform thermal condition.

If we do not want to confine our attention to fluid bodies enclosed in a vessel, then insight into the following discussions may be rendered more easy by supposing the body investigated to be surrounded by an elastic envelope which, under the assumed equilibrium, exerts everywhere an equal pressure upon the surface elements in directions normal to these elements. Now if we supply from without the infinitesimal quantity of heat  $dQ$  measured in heat-units, the following changes will occur in the state of the body.

First: There will occur an increase in the molecular motion; the smallest parts of the body oscillating about their positions of equilibrium experience changes of velocity and changes in their distances from the positions of equilibrium, in consequence of which the work stored in the sum total of all the molecular motions experiences a change. Let  $dW$  designate the increment of energy of this molecular motion expressed in units of work (meter-kilograms) [foot-pounds].

Secondly: There will occur a change in the mid-positions of the smallest parts of the body, whose distances apart may be regarded as very great in comparison with the amplitude of the oscillations. But since these parts act upon one another with certain forces, a change of position will be connected with an expenditure of work, a change of energy of position, i.e., of potential energy. Let this quantity of work in the sense of expenditure be designated by  $dJ$ .

Thirdly: There will occur a change in the total volume of the body. If we here consider expansion as taking place, then external pressure acting from the outside against the surface of the body will be overcome, the infinitesimal expansion corresponding to a quantity of work designated by  $dL$ .

Now these three quantities of work just defined stand, according to the principles given in the Introduction, in a simple rela-

tion to the quantity of heat  $dQ$  which is absorbed during the assumed change of state. If we designate by  $A$  (measured in heat-units) the quantity of heat which disappears or is generated when a unit of work (meter-kilogram) [foot-pound] is gained or lost, then in the case before us the work performed,  $dW + dJ + dL$ , corresponds to a heat consumption of the amount  $A(dW + dJ + dL)$ , and we get as the starting-point for all further investigation the equation

$$dQ = A(dW + dJ + dL). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this equation  $A$  means a constant value, according to the Introduction, and is to be taken as 1:424 [1:772.83]; that in special cases some of the terms of the preceding equation may become zero or negative is self-evident. The positive and negative signs of  $dQ$  will respectively signify heat supply or heat withdrawal, while a positive sign for  $dL$  will indicate an increment of volume (expansion), and a minus sign will indicate a decrement of volume (compression).

We must not overlook the fact that the foregoing equation is true only under the several limitations specified above. To be sure, the following investigation will show that in certain cases we can drop some of the specially made assumptions and extend and transform equation (1) under the assumptions that chemical changes simultaneously occur, but for the present we will disregard such cases.

## § 2. THE INNER WORK OR ENERGY OF THE BODY.

As already mentioned, the changes of state of a body are completely determined by the changes of volume and of pressure as soon as we assume the mass of the body to be of unit weight.

If we designate "specific volume" by  $v$  and "specific pressure," in the sense indicated, by  $p$ , then we ought to try to transform equation (1) by expressing the individual terms of the right member by the magnitudes  $p$  and  $v$ . Such a transformation cannot be carried out because we have not succeeded (without hypothetical assumptions) in establishing a relation between the first and sec-



ond terms of the right-hand side of equation (1) and the two variables  $p$  and  $v$ . Therefore the second term is combined with the third or it is combined with the first term; both kinds of transformation were first given by Clausius.<sup>1</sup> If we make the substitution  $dJ + dL = dH$ , then we get from equation (1):

$$dQ = A(dW + dH). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We can therefore say that the heat  $dQ$  imparted to the body is expended in two ways: the one part,  $AdW$ , is expended in increasing the energy of the molecular motion, in increasing the work which resides in the sum total of the smallest parts in consequence of their oscillations about positions of equilibrium. We assume that this part of the supplied heat expresses itself as an increase of the sensible heat (shown by thermometers). On the other hand the second term,  $AdH$ , of equation (2) corresponds to the work  $dH$  which is expended during the change of position of the smallest parts in overcoming not only the forces with which the parts act upon one another, but at the same time in changing the total volume by overcoming the external pressure acting on the surface of the body; according to Clausius this may be expressed by saying that the work  $dH$  or its part  $AdH$  of the supplied heat is expended in changing the disgregation.

The second of the two mentioned transformations of equation (1) is much the more fruitful one. If we place  $dW + dJ = dU$ , then we get

$$dQ = A(dU + dL), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and it is this expression which will serve as a starting-point for all the following investigations. The heat imparted to the body can be divided into two parts; the part  $AdU$  embraces the increment  $dU$  of the kinetic and of the total potential energy, while the second part corresponds to the heat value  $AdL$  of the work which is expended in expanding the body against the external pressure acting against the surface, and is to be regarded as the, to the eye, visible effect of the absorption of heat.

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<sup>1</sup> Clausius, Abhandlungen, etc., 1864. See also his treatise "Die mechanische Wärmetheorie." Brunswick, 1876.

The first-mentioned part  $dU$  includes, according to the foregoing, the total work which has been done within the body; therefore in what follows the value  $U$  will be called the inner work, the intrinsic energy or simply the energy of the body.<sup>1</sup> Under the special assumptions made in establishing equation (1) the inner work  $U$  for a given body is completely determined by the pressure  $p$  and the volume  $v$  (of the unit of weight) and must therefore be capable of representation by a function of  $p$  and  $v$ .

Accordingly if we put

$$U = F(p, v), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

differentiation gives

$$dU = \frac{\partial U}{\partial p} dp + \frac{\partial U}{\partial v} dv,$$

and if we respectively designate by  $X$  and  $Z$  the two partial differential coefficients, that is, put

$$X = \frac{\partial U}{\partial p} \quad \text{and} \quad Z = \frac{\partial U}{\partial v},$$

then we can write in simpler fashion

$$dU = Xdp + Zdv; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

but here there exists between the functions  $X$  and  $Z$ , according to the Principles of the Differential Calculus, the relation

$$\frac{\partial X}{\partial v} = \frac{\partial Z}{\partial p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

a relation of which use will be made in the following investigation

The finding of the form of the function given in equation (4) constitutes the main aim of all the following investigations.

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<sup>1</sup> Kirchhoff calls the quantity  $U$  with a negative sign "acting function"; Clausius understands by inner work only that part of equation (1) which is designated by  $dJ$  in this text.

### § 3. THE EXTERNAL WORK.

The second term  $dL$  of equation (3) gives the work which is expended during the infinitesimal expansion of the body in overcoming the external pressure; we call this value  $dL$ , but if we have to do with a finite expansion we call it  $L$  (following Clausius), the "external work"; but here we at first hold fast to the assumption that the pressure  $p$  remains the same at all parts of the body during change of volume, and moreover is equal to the pressure exerted from the outside upon the surface of the body (say, for example, by the surrounding envelope). If we designate the pressure in the interior, and consequently the pressure exerted by the body from within against the external envelope, as "body tension," and, conversely, the pressure by the envelope against the body's surface as the external pressure, then we assume that during the change of state of the body there is constantly equilibrium between the body tension and the external pressure, and therefore the value  $p$  holds for the one pressure as well as for the other; if we suppose the body to experience an increment of volume during heat absorption, that is, an extension or expansion, then the supposition made is valid only under the assumption that extension takes place slowly and uniformly, and consequently that the surface elements advance outward slowly and uniformly in the direction of their normals; during decrement of volume or compression of the body the motion of the surface elements takes place in the reverse direction, toward the inside.

Under the circumstances mentioned the quantity of work  $dL$  can be easily expressed in terms of  $p$ ,  $v$ .

If we designate the surface elements by  $f_1, f_2, f_3$ , etc., and the infinitesimal displacements of the body by  $s_1, s_2, s_3$ , etc., then the pressure from without against the individual elements of the area is  $f_1p, f_2p, f_3p$ , etc., and since these pressures during the infinitesimal displacements can be regarded as constant, we will have for the separate quantities of work  $f_1ps_1, f_2ps_2, f_3ps_3$ , etc., and their sum represents the whole work  $dL$  expended in overcoming the

external pressure; consequently we have the relation

$$dL = p[f_1 s_1 + f_2 s_2 + f_3 s_3 + \dots].$$

But now the expression in the bracket is simply the increment of the total volume  $v$  of the unit of weight of the body, and therefore we have the relation

$$dL = p dv, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and by substituting in equation (3) we get

$$dQ = A(dU + p dv). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If we consider a finite change of state and designate the initial pressure and specific volume by  $p_1$  and  $v_1$ , then, according to equation (4), the value of the inner work at the beginning is  $U_1 = F(p_1, v_1)$ , and at the end  $U_2 = F(p_2, v_2)$ , and we get from equation (8), with the help of (7), the whole heat supplied,

$$Q = A(U_2 - U_1 + L), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or

$$Q = A[F(p_2, v_2) - F(p_1, v_1) + \int_{v_1}^{v_2} p dv]. \quad . \quad . \quad . \quad (10)$$

The first two terms of the right-hand side of this equation are completely determined by the initial and final state of the body, provided the form of the function  $U = F(p, v)$  is known; it is not so with the third term, which represents that part of the heat expended in external work. In carrying out the integration indicated in equation (10) it is still necessary to know the manner in which, during the whole course of the heat supply, the body tension and the external pressure  $p$  (which we must repeatedly emphasize are to be here regarded as identical) vary with the volume, and in turn this variation depends on the manner in which the heat supply takes place in all parts of the process considered.

If, for a particular case, the law is known, according to which the pressure  $p$  changes with the volume, then the changes of state can be very simply shown to the eye in a graphical way; namely, if we lay off as abscissa the value of specific volume  $v$  at any

instant, and as ordinate the corresponding pressure  $p$  (Fig. 1). then the state of the body at the instant in question is completely

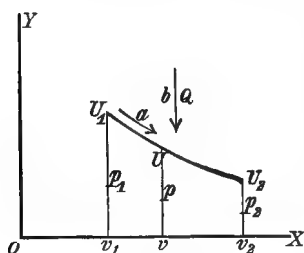


FIG. 1.

determined by the location of the point  $U$ , and the curve  $U_1U_2$ , which we will hereafter designate as pressure curve, shows also the way in which the passage from the initial condition  $U_1$  into the final condition  $U_2$  takes place; the direction of this change can, moreover, be shown by an arrow  $a$  drawn in the direction of the curve  $U_1U_2$ ; if this passage is connected with a supply of heat this will hereafter be shown by a second arrow,  $b$ , directed toward the curve  $U_1U_2$ . If the figure is to indicate that heat withdrawal occurs, then we simply reverse the direction of the arrow in all the corresponding presentations; likewise the reversal of the arrow  $a$  will indicate the passage from the state  $U_2$  to the state  $U_1$ , that is, show a compression of the body. At the beginning and end of the process we always assume the condition of rest to obtain; now, if we are to start from the point  $U_1$ , it is only necessary to assume for the introduction of slow and uniform expansion that the external pressure diminishes a little for an instant. On the other hand, with the path reversed, during compression, we take  $U_2$  as a starting-point, and assume that its external pressure momentarily increases a little; during the whole path of the expansion  $U_1U_2$  or of the compression  $U_2U_1$  there will then be equilibrium between the body tension and the external pressure, and we can carry out the process either in going from  $U_1$  to  $U_2$  or in the reverse direction,  $U_2$  to  $U_1$ . During the reversal the arrows of the figure change their direction, and in equations (9) and (10) all terms change their signs; therefore if heat supply occurred during the forward motion, there will be heat withdrawal in all parts of the return motion, and if during the forward motion the external work  $L$  is performed, then during the return motion this work will have to be expended. Such a process is called a reversible one, and this term expresses most briefly that during

change of state of a body there is constantly equilibrium between the external pressure and the body tension.

The external work

$$L = \int_{v_1}^{v_2} p \, dv$$

of equations (9) and (10) is here represented simply by the area in Fig. 1 bounded by the pressure curve  $U_1U_2$  and the two end ordinates. This quantity of work depends only upon the course of the pressure curve; but as an infinite number of pressure curves can be drawn through two given points  $U_1$  and  $U_2$ , there will exist for each of these curves an external work  $L$  of different value, and consequently there will likewise vary the quantity of heat  $Q$  which, according to equations (9) and (10), is to be imparted to the body for the assumed passage.

Only that part of the heat supply which is expended on inner work is completely determined solely by the initial and the final states. This important proposition, which was first definitely enunciated by C l a u s i u s, furnishes the important starting-point of the mechanical theory of heat; up to his time it was usually assumed in Physics, generally without further explanation, that the quantity of heat which was to be supplied to a body for certain changes of state was completely determined by its initial and its final states  $(p_1, v_1)$  and  $(p_2, v_2)$ , while we now know that there should also be given the path along which the passage occurs. Expressed mathematically equation (8),

$$dQ = A(dU + p \, dv),$$

is an incomplete differential; the integration can only be effected when we also know in what manner the heat supply varies and how the state of the body varies with the pressure  $p$  and the volume  $v$ .

#### § 4. DERIVATION OF THE FIRST FUNDAMENTAL EQUATION.

If in the just-quoted equation we substitute for the change of inner work that given by equation (5), in which  $X$  and  $Z$  are those functions of  $p$  and  $v$  which represent the partial differential coefficients of the inner work  $U$  with respect to  $p$  and  $v$ , that is, substitute

$$dU = X dp + Z dv, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

we get

$$dQ = A[X dp + (Z + p)dv].$$

Because all the following deductions will be simplified thereby we here put

$$Z + p = Y; \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

then we can write

$$dQ = A(X dp + Y dv). \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If we differentiate equation (12) on both sides with respect to  $p$ , we have

$$\frac{\partial Z}{\partial p} + 1 = \frac{\partial Y}{\partial p},$$

and then utilizing equation (6), p. 27,

$$\frac{\partial Y}{\partial p} - \frac{\partial X}{\partial v} = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

This equation may be designated as the **first fundamental equation**. It was first given by Clausius, though in different form, and is simply an analytical expression for the fact that equation (13) is an "incomplete differential," otherwise the right member of the first fundamental equation (I) would be equal to zero instead of being equal to unity. Since equation (13) followed from equation (8), and the latter was already recognized in the preceding investigation as an incomplete differential, we see that what is given in equation (I) simply expresses in mathematical form what was before elucidated in words.

## § 5. DERIVATION OF THE SECOND FUNDAMENTAL EQUATION. \*

The continuation of the general investigation demands the introduction of two more functions which, it will be seen later, assume a prominent significance in the theory of heat. Let  $S$  designate one of these functions, and let its relation to  $p$  and  $v$  be represented in general form by

$$S = f(p, v). \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now if we divide both sides of the just given equation (13) by  $AS$ , we get

$$\frac{dQ}{AS} = \frac{X}{S} dp + \frac{Y}{S} dv. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

We can now so choose the form of function  $S$  that the right member of this equation will become a complete differential; that is to say, this expression will seem to have proceeded from the differentiation of another function:

$$P = \phi(p, v), \quad . \quad . \quad . \quad . \quad . \quad (16)$$

so that we have the relation

$$\frac{dQ}{AS} = dP, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

or

$$dQ = AS dP. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

But these assumptions completely fix mathematically the significance of the two functions  $S$  and  $P$ ; the function  $S$  appears here as the integrating factor <sup>1</sup> of the right-hand side of equation

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\* Remark.—It ought to be emphasized that there are an infinite number of functions which, like  $S$ , possess the property of rendering expression (15) a complete differential. If we imagine both sides of equation (17) to be divided by  $f(P)$ , any arbitrary function of  $P$ , we get

$$\frac{dQ}{ASf(P)} = \frac{dP}{f(P)}.$$

Now since here the right member can be integrated, it follows that the left member can likewise be integrated, and therefore we can regard generally the



(13), and its connection with the functions  $X$  and  $Y$  through equation (15), according to the Principles of the Calculus, is given by the formula

$$\frac{\partial}{\partial v}\left(\frac{X}{S}\right) = \frac{\partial}{\partial p}\left(\frac{Y}{S}\right).$$

If we carry out the indicated differentiation, we get

$$S \frac{\partial X}{\partial v} - X \frac{\partial S}{\partial v} = S \frac{\partial Y}{\partial p} - Y \frac{\partial S}{\partial p},$$

or also

$$S \left( \frac{\partial Y}{\partial p} - \frac{\partial X}{\partial v} \right) = Y \frac{\partial S}{\partial p} - X \frac{\partial S}{\partial v}.$$

But since, according to the first fundamental equation (I), the expression in the parenthesis is equal to unity, we have

$$S = Y \frac{\partial S}{\partial p} - X \frac{\partial S}{\partial v}, \quad . . . . . \text{ (II)}$$

expression  $Sf(P)$  as the integrating factor. Here  $f(P)$ , the arbitrary function of  $P$ , can be put equal to unity, as is done in the text. If in future applications another choice of this function presents advantages, then we can at any time make use of the foregoing proposition.

Thus we can put  $f(P)$  equal to any constant  $k$ , so that we can ascribe to the value  $kS$  all the properties which the future applications in the text may find for the function  $S$  itself. It is just this last generalization of which profitable use will be made hereafter.

The step taken in the text, introduction of function  $S$  as integrating factor, was first taken in the second edition of the present book, 1866. R. Rühlmann notes in his article "Geschichte der mechanischen Wärmetheorie," at the end of the second volume of his "Handbuch der mechanischen Wärmetheorie," Brunswick, 1885, that before him the same course had been pursued by Reech (Journal de Mathématiques pures et appliquées von Liouville, 2d Series, Vol. I, 1856, p. 58); but this remark is entirely incorrect. In the first edition of the present book (1860), I, of course, giving credit to the source in discussing the second fundamental law, pursued Reech's course, and that is also incidentally mentioned by Clausius; the latter's remark was doubtless sufficient reason for R. Rühlmann not to examine more closely Reech's work. Reech from the very start proceeds from the assumption that  $S$  is a function of the temperature, and at that time furnished nothing which was not already known through Clausius. It was not until the second edition that I pursued the above-mentioned course; this course at first avoids every assumption concerning the physical significance of said function, and herein lies the difference upon which, in my opinion, great weight should be laid.

and this may be put down as the second fundamental equation of Thermodynamics. It was first developed by Clapeyron,<sup>1</sup> and later in another form by Clausius, and both give from the start the particular physical significance to the function  $S$  to which the following investigation will likewise lead, but which cannot be obtained without setting up a new principle. It therefore seems to me more suitable to base the general discussions for the present exclusively on the first fundamental law (the equivalence of heat and work). Now if we find from equation (II) first  $Y$  and then  $X$ , and substitute the values in equation (13), at the same time making use of the relation

$$dS = \frac{\partial S}{\partial p} dp + \frac{\partial S}{\partial v} dv, \quad . . . . . (19)$$

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<sup>1</sup> E. Clapeyron, Engineer of Mines (born Feb. 21, 1779, died Jan. 28, 1864). "Mémoire sur la puissance motrice de la chaleur," Journal de l'école polytechnique. Twenty-third Number, Vol. XIV, Paris, 1834. It appeared as a German translation first in 1843 in Poggendorff's Annalen," Vol. 59, pp. 446 and 566. This masterly discussion by Clapeyron, which is distinguished by great clearness and elegance in the mathematical presentation, is moreover the first mathematical work on Thermodynamics, and is based on the formerly very rare work of Sadi Carnot (born June 1, 1796; died Aug. 24, 1832), "Réflexions sur la puissance motrice du feu," Paris, 1824.

Both works were for a long time unnoticed, or at least unused, and their high value was only recognized later through the discussions of Clausius, of which the first appeared in 1850.

The work of Carnot was reprinted in the "Annales scientifiques de l'École normale supérieure," 1872 (II. series, Vol. I) and more recently (1878) was published separately in Paris by Gauthier-Villars under the original title. This issue contains interesting biographical notices, extracts from the papers which Carnot left behind him, and was in 1878 presented to the Paris Academy of Sciences by his younger brother, Senator H. Carnot. The most remarkable statement in these papers is the following one, which was reproduced in facsimile in the aforesaid issue:

"D'après quelques idées que je me suis formées sur la théorie de la chaleur, la production d'une unité de puissance motrice nécessite la destruction de 2.70 unités de chaleur." Here Carnot understands by unit of work that which is necessary to raise 1 cbm. of water to the height of 1 meter. His unit is therefore 1000 mkg; the unit of heat would therefore correspond to

$$\frac{1000}{2.70} = 370 \text{ mkg,}$$

and this is almost exactly the same value as was found by J. R. Mayer (1842) for the mechanical equivalent of heat, of course with the statement of the method by which it was obtained (Mayer gives 365 mkg).

then we will get the second and third of the following three equations:

$$\left. \begin{aligned} dQ &= A[X dp + Y dv], \\ dQ &= \frac{A}{\frac{\partial S}{\partial p}} [X dS + S dv], \\ dQ &= \frac{A}{\frac{\partial S}{\partial v}} [Y dS - S dp]. \end{aligned} \right\} \dots \dots \dots \text{(III)}$$

For the purpose of ready inspection we will here reproduce equations (8) and (18),

$$dQ = A[dU + p dv]$$

and

$$dQ = AS dP.$$

These five equations are identical and differ from one another in having a different independent variable in each equation. The utilization of these formulas is only possible if the form of the functions  $X$ ,  $Y$ ,  $S$ , and  $P$  is known. But if we review the course of the present work, we recognize that it is only necessary to determine one of the designated functions in order to determine the remainder from the given relations.

For example, if the form of the function  $S = f(p, v)$  is in any way known, then functions  $X$  and  $Y$  can be determined from the two fundamental equations (I) and (II). The substitution of  $Y$  in equation (12) then gives  $Z$ , and the integration of equation (11) thereupon brings out function  $U$ . Finally, the last function,  $P$ , results when we integrate equation (15) and make use of equation (18).

The line of thought here indicated is the one which we will now pursue, but the determination of the function  $S$  will demand a series of preliminary investigations whose results are separately of consequence in future applications, namely, in the solution of certain physical and technical problems.

## § 6. INVESTIGATION OF DIFFERENT PRESSURE CURVES.

If a body while absorbing heat passes from the initial condition  $a$  (Fig. 2), where its initial pressure is  $p_1$  and initial volume  $v_1$ , to the final condition  $b$  ( $p_2, v_2$ ) along the pressure curve  $ab$  which represents a reversible path, then the equation of the pressure curve can be represented by

$$R = \phi(p, v), \quad . \quad . \quad (20)$$

provided the magnitude  $R$  can be regarded as a constant. The corresponding constant can be found if we

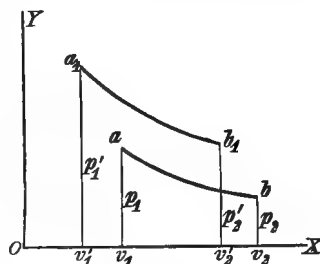


FIG. 2.

substitute in this equation for  $p$  and  $v$  the initial values  $p_1$  and  $v_1$ ; for another initial point,  $a_1$ , equation (20) gives a pressure curve of the same sort, but for this the constant has a different value, and indeed for the new curve we should put  $R' = \phi(p_1', v_1')$ , while for the first curve we should write  $R = \phi(p_1, v_1)$ . Equation (20) therefore represents in general the curve equation of an infinite series of pressure curves of the same species which differ only by the different values of their constant  $R$ ; and for a point  $a$  of the plane given by its coordinates  $p_1$  and  $v_1$  there is simultaneously determined through the corresponding constant the special pressure curve passing through  $a$ . Now if we use equation (20) in formula (10), we can compute the quantity of heat  $Q$  which is to be imparted along the corresponding pressure curve during the passage from  $a$  to  $b$ ; similarly when  $Q$  is negative this quantity of heat is to be withdrawn, and we at once see that the sign of  $Q$  is the same when bodies starting from the initial condition  $a, a_1$ , etc., describe separate pressure curves of the same species in the same direction. Accordingly if heat supply was necessary along the path  $ab$  (Fig. 2), then such supply will also be necessary along the path  $a_1b_1$ ; on the other hand, if we had transferred the body from the state  $b$  to the state  $b_1$  and by reversing brought it from  $b_1$  to  $a_1$ , then along this path  $b_1a_1$  a certain quantity of heat

would have to be withdrawn, provided heat supply had taken place before along the path  $ab$ , and conversely.

If the two pressure curves of the same species  $ab$  and  $a_1b_1$  are infinitesimally near to one another, then their constants will differ by the infinitesimal  $R$ , which, according to equation (20), will be

$$dR = \frac{\partial R}{\partial p} dp + \frac{\partial R}{\partial v} dv.$$

Of the numberless pressure curves of different species which can be considered there are especially three which play an important part in all future developments, and these will now receive fuller discussion.

We discussed before, with some detail, the significance of the three functions:

$$U = F(p, v), \quad S = f(p, v), \quad \text{and} \quad P = \phi(p, v).$$

If the body in state  $a$  is given by the pressure  $p_1$  and volume  $v_1$ , then there exists for this point a definite value for each of the three functions, respectively:

$$U_1 = F(p_1, v_1), \quad S_1 = f(p_1, v_1), \quad \text{and} \quad P_1 = \phi(p_1, v_1).$$

Accordingly in Fig. 3 we have, starting from point  $a$ , three curves  $aU_1$ ,  $aS_1$ , and  $aP_1$ , provided heat supply and pressure variation are so arranged that at one time  $U$ , another time  $S$ , and the third time  $P$  is maintained constant.

The first of the three curves mentioned is subject to the relation

$$F(p, v) = U_1, \quad . \quad . \quad . \quad (21)$$

which expresses that during the change the inner work (energy) is kept constant.

Therefore  $dU = 0$ , and the quantity of heat which is necessary along the path  $ab$  to effect the change to the final condition  $(p_2, v_2)$  can be found from equation (3), page 26,

$$Q = AL,$$

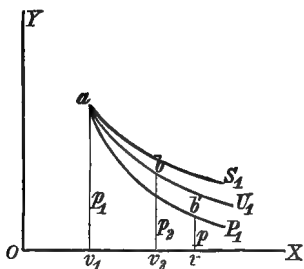


FIG. 3.

where  $L$  is understood to be the external work which, in Fig. 3, is given by the area  $abv_2v_1$ . The corresponding curve may be called (according to Cazin) the "isodynamic curve," and for this we can say that during the expansion of the body, according to this curve, the whole heat supply is converted into outer work, and conversely that during compression the outer work expended has been converted into heat, and as such must be completely withdrawn. With the second curve  $aS_1$  (Fig. 3) it is assumed that the function  $S$  is to be maintained constant; the equation of the curve is therefore

$$f(p, v) = S_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and this curve, for reasons which will be given later, will be called the isothermal curve.

Finally, with the third curve  $aP_1$ , the function  $P$  is to remain constant during the changes of state; the equation of the curve is therefore

$$\phi(p, v) = P_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Since  $P = P_1$  is a constant, there follows  $dP = 0$ , and therefore from the equation accompanying set (III), namely,

$$dQ = AS \, dP,$$

we also get  $dQ = 0$ . It follows from this that equation (23) represents those changes of state of the body which occur if during the whole course heat is neither supplied nor withdrawn. The corresponding curve we will in the following call the adiabatic curve, or briefly the adiabatic, as was done by Rankine (born July 5, 1820, and died Dec. 24, 1872).

If there is adiabatic expansion along the path  $ab'$  (Fig. 3) from the condition  $(p_1, v_1)$  to the final condition  $(p, v)$ , and  $U_2$  is the inner work corresponding to the point  $b'$ , then if we integrate equation (3), that is to say,

$$dQ = A(dU + dL),$$

we get, because  $dQ=0$ , and also  $Q=0$ ,

$$0=A(U_2-U_1+L),$$

from which follows the external work

$$L=U_1-U_2,$$

which is represented by the area  $ab'vv_1$ .

In accordance with the foregoing discussion we will hereafter briefly speak of isodynamic, isothermal, or adiabatic expansion (or compression), according as one or the other of the three discussed changes of state are in question.

The last of the preceding equations therefore expresses that during adiabatic expansion the outer work requires an expenditure of an equal amount of inner work, and conversely that during adiabatic compression the expended outer work finally completely reappears in the form of increased inner work.

## § 7. GRAPHICAL DETERMINATION OF HEAT QUANTITIES.

To what has been said there may be added a few important remarks.

If we imagine the body in state  $a$  to be given by  $p_1$  and  $v_1$  (Fig. 4), and supply it along the path  $ab$  with a quantity of heat  $Q$  till it has passed into the final state  $b$ , determined by  $p_2$  and  $v_2$ , then its initial condition  $a$  will be given by the value  $U_1=F(p_1, v_1)$ , and its final condition  $b$  by the value  $U_2=F(p_2, v_2)$ , provided the function  $U=F(p, v)$  is known. From equation (3), page 26, we can now find the quantity of heat  $Q$  which must be supplied along the arbitrarily assumed curve  $ab$ :

$$Q=A(U_2-U_1+L), \quad . \quad . \quad . \quad . \quad (24)$$

where  $L$  represents the external work, which is given by the area  $abv_2v_1$ .

But to the two states  $a$  and  $b$  there correspond the perfectly definite values of the function  $P$ ; that is, if we assume this func-

tion as known, then  $P_1 = \phi(p_1, v_1)$  and  $P_2 = \phi(p_2, v_2)$ , and thus we have the means of drawing the two adiabatics  $P_1 a P_1$  and  $P_2 b P_2$  (Fig. 4) passing through the two\* points  $a$  and  $b$ , for the equations of both can be written

$$\phi(p, v) = P_1 \quad \text{and} \quad \phi(p, v) = P_2.$$

Furthermore, let us consider the body to exist in any state  $a_0$  corresponding to the values  $p_0$  and  $v_0$ ; if the corresponding value of the inner work  $U_0 = F(p_0, v_0)$  is computed, then we can draw through this point the isodynamic curve  $a_0 U_0$ , whose equation is  $U_0 = F(p, v)$ , and whose curve will cut the two adiabatics in the points  $c$  and  $d$ , having the pressure and volume  $p_1', v_1'$  and  $p_2', v_2'$  respectively.

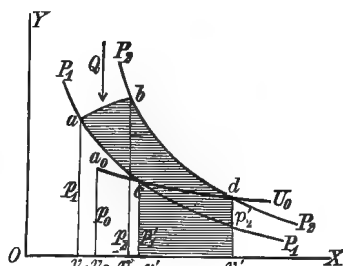


FIG. 4.

Now if we imagine the body to be brought back into the initial state  $a$  and allow it to expand adiabatically from  $a$  to  $c$ , then because  $dQ = 0$  and  $Q = 0$ , we get from integration of equation (3)

$$0 = A(U_0 - U_1 + L_1),$$

the outer work  $L_1$  being represented by the area  $a c v_1' v_1$ .

On the other hand if we imagine the body to pass adiabatically from the state  $b$  to the state  $d$ , we have in like manner, for this change,

$$0 = A(U_0 - U_2 + L_2),$$

where the outer work  $L_2$  is determined by the area  $b d v_2' v_2$ .

If we subtract the last two formulas from each other we get

$$U_2 - U_1 = L_2 - L_1,$$

and substitution in equation (24) then gives for the passage from  $a$  to  $b$  the quantity of heat:

$$Q = A(L + L_2 - L_1).$$



If we further introduce for the separate quantities of work in the parenthesis the areas of Fig. 4 which represent them, we get the simple result that the hatched area  $abd v_2' v_1' ca$  of the figure represents the value  $L + L_2 - L_1$ , or the value of the quantity of heat  $Q$ , measured in units of work, which is necessary for the change of state along the pressure curve  $ab$ .

We have here acquired a simple graphical procedure for ascertaining the quantity of heat  $Q$  for the change of state  $ab$  given by the diagram, provided that for the body in question we know the general course of the adiabatic and of the isodynamic curve.

It is here worth noting that the position of the point  $a_0$ , through which the isodynamic curve  $U_0$  is passed, can be chosen in a perfectly arbitrary manner; but the two adiabatics are fixed, one of them passes through the initial point  $a$ , and the other through the final point  $b$ .

We now recognize clearly from the figure the influence exerted by the kind of passage along the curve  $ab$  both on the outer work  $L$  and upon the heat supplied; this was already fully described at the beginning of the general investigation; every different pressure curve running from  $a$  to  $b$  leads to different values of  $L$  and  $Q$ .

If we let the point  $a_0$ , through which the isodynamic curve  $U_0$  was passed, coincide with the initial point  $a$  (Fig. 4), then this special assumption will lead us to the graphical representation first given by Cazin.<sup>1</sup>

On the other hand if we so choose  $a_0$  that the intersections  $cd$  can coincide with the axis of abscissas  $OX$ , then we get the method given by Macquorne Rankine<sup>2</sup>; in this case the heat quantity  $Q$  expressed as work is represented simply by the area included between the pressure curve  $ab$  and the two adiabatics; to be sure, Rankine here assumes that both adiabatics approach the axis of abscissas as asymptotes, which can be regarded as correct at least for gases and vapors.

Hereafter, the more general representation of Fig. 4 will

<sup>1</sup> Cazin, "Théorie élémentaire des machines à air chaud." Versailles, 1865.

<sup>2</sup> Macquorne Rankine, "A Manual of the Steam-engine and other Prime Movers." London and Glasgow, 1859.

be utilized in some discussions, but we may here and now remark that subsequent discussions will lead to a still simpler graphical method which is to be preferred in the treatment of technical problems. In drawing the diagram of Fig. 4 a difficulty is encountered; namely, it will be seen that with certain bodies (gases and vapors) the course of the adiabatic curve deviates but little from that of the isodynamic curve; the intersections *c* and *d* of the curves mentioned in Fig. 4 consequently occur at very acute angles, and therefore these points cannot be fixed with sufficient accuracy by the drawing of the curves. The same difficulty exists in the method given by Cazin mentioned above. The third method by Rankine, likewise indicated above, can be seen at once to be useless for the graphical solution of our problems because it demands the determination of the contents of an area enclosed by two curves which approach one another as asymptotes.

## § 8. RELATION BETWEEN THE FUNCTIONS S AND P.

If a body receiving heat passes from the initial condition  $a_1(p_1, v_1)$  (Fig. 5), along any arbitrary but reversible path  $a_1b_1$  to the condition  $b_1(p_2, v_2)$ , there will follow from

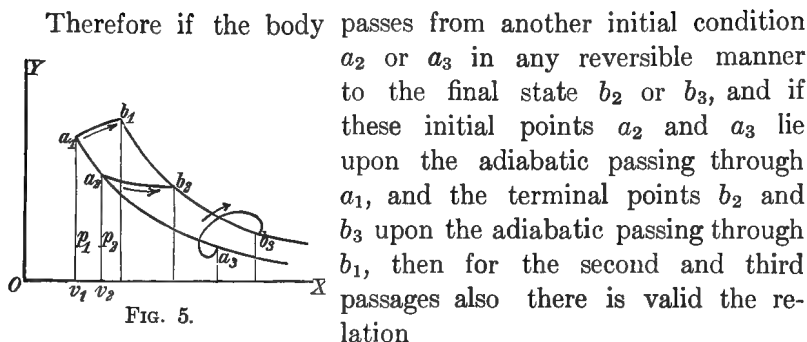
$$\frac{dQ}{AS} = dP$$

by integration

$$\int \frac{dQ}{AS} = P_2 - P_1,$$

where, according to equation (16), the value  $P_1$  corresponding to point  $a_1$  is determined by the relation  $P_1 = \phi(p_1, v_1)$ ; in like manner there corresponds to the point  $b_1$  the value  $P_2 = \phi(p_2, v_2)$ .

Now if we pass through the points  $a_1$  and  $b_1$  two adiabatic curves, then for the former, as was mentioned on page 39, the value of function  $P = \phi(p, v)$  is the same for all points, namely,  $= P_1$ , and likewise for the adiabatic passing through  $b_1$  the corresponding value for  $P$  is constant for all points, and equal to  $\phi(p, v) = P_2$ .



$$\int \frac{dQ}{AS} = P_2 - P_1.$$

From this follows the important proposition:

“If a body in any (reversible) way passes from one point of a particular adiabatic to any other point of a second adiabatic, then the integral

$$\int \frac{dQ}{AS},$$

taken between the same limits, has always one and the same value.”

If, for simplicity, we designate the difference  $P_2 - P_1$  by  $P$ , we have the magnitude

$$P = \int \frac{dQ}{AS}, \quad . . . . . (26)$$

a constant quantity for every one of the infinite number of passages possible. For the return path the proposition likewise holds; but then the sign of  $P$  changes and will be negative, provided it was positive upon the forward path, and conversely.

We recognize from this that in Thermodynamics the adiabatic curves play a part similar to the altitudes, or differences of level in Mechanics. For reasons which will appear in the following discussions I have called the value  $P$  represented by equation (26)

"heat weight";<sup>1</sup> but we will also hereafter use for it the term "entropy," one which is more widely used among physicists.

In discussing, in Fig. 5, the passage of a body from one adiabatic to another, the pressure curves were assumed running in a perfectly arbitrary manner; we can now think of the transfer as taking place upon particular prescribed curves, and here that case is of special significance in which the transfer takes place along the isothermal curve, i. e., along the curve for which the function

$$S = f(p, v)$$

is kept constant.

If the body subjected to investigation exists in the state  $a_1$  (Fig. 6), it will possess for this a particular value  $S_1$  of the function  $S$ , namely,  $S_1 = f(p_1, v_1)$ ; now, if we bring the body to the state  $b_1$  and at the same time supply heat to the body along the isothermal curve of constant value  $S = S_1$ , that is, along the curve having the equation

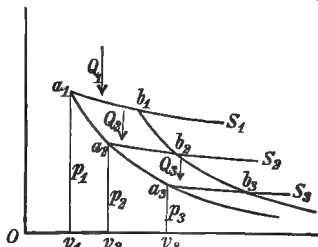


FIG. 6.

$$S_1 = f(p, v),$$

then equation (26) can be integrated, and, designating by  $Q_1$  the necessary quantity of heat, we have

$$Q_1 = APS_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

If we again pass adiabatics through the point  $a_1$  and  $b_1$ , and imagine this same body at one time to start from the point  $a_2$  and at another time from the point  $a_3$ , both of these points lying upon

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<sup>1</sup> Clausius designates the integral  $\int \frac{dQ}{S}$ , with the addition of a constant, as the transformation value or as the entropy of a body in which  $S$  appears as the temperature function, and as such it will likewise appear in the subsequent developments of the present treatise. (Compare quotation on page 24.)—Rankine calls  $P = \phi(p, v)$  the thermodynamic function.—C. Neumann designates  $P$  as the parameter of the caloric (adiabatic) curves. ("Vorlesungen über die mechanische Theorie der Wärme." Leipsic, 1875.)

the first adiabatic, and to proceed along the corresponding isothermals to the second adiabatic, and if, furthermore,  $Q_2$  is the heat supplied for the path  $a_2b_2$ , and  $Q_3$  that for the path  $a_3b_3$ —then, according to equation (27), we will have the relations

$$Q_2 = APS_2 \quad \text{and} \quad Q_3 = APS_3.$$

From this, and from equation (27), it follows that for all passages the heat weight is constant, namely,

$$P = \frac{Q_1}{AS_1} = \frac{Q_2}{AS_2} = \frac{Q_3}{AS_3}. \quad \cdot \cdot \cdot \cdot \cdot \quad (28)$$

The necessary quantities of heat are, therefore, proportional to the corresponding values of  $S$ .

Use will be made hereafter of the foregoing relation (28).

## § 9. REVERSIBLE CYCLES.

For the quantity of heat which must be imparted to a body undergoing changes of state along the reversible path, in order that the body may pass from a certain initial condition  $a$  into a given final condition  $b$ , we found from Fig. 4 and equation (24), page 38,

$$Q = A(U_2 - U_1 + L).$$

But now if we suppose that the assumed pressure curve is a closed curve (Fig. 7a), and that, consequently, the final state coincides with the initial state, the point  $b$  with the point  $a$ , then in the foregoing formula we have  $U_1 = U_2$  and get the simple relation

$$Q = AL. \quad \cdot \cdot \cdot \cdot \cdot \quad (29)$$

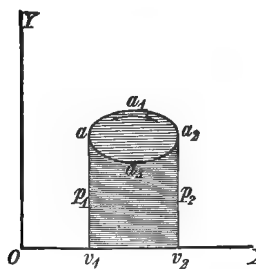


FIG. 7a.

Here  $L$  means the work gained, which is measured by the area enclosed by the pressure curve, and  $Q$  is the quantity of heat consumed in producing it. But doubtless this quantity of heat can be imparted,

during the whole process, only from without, that is, be furnished by other bodies, and therefore can not, either in whole or in part, be abstracted from the interior of the body with which the cycle was described, for, according to the hypothesis, the body has been led back to its initial condition: its total inner work is, consequently, the same at the end of the process as at the beginning.

A process of the contemplated sort is called (according to Clausius) a cycle, and, moreover, since we are at first considering only reversible changes of state, it is called a reversible cycle.

The closer consideration of Fig. 7a shows, moreover, that the work gained can be considered as consisting of two parts: during the expansion of the body along the path  $aa_1a_2$ , there was gained the work  $L_1$  represented by the total hatched area; and when led back, or during compression along the path  $a_2a_3a$ , there was expended the work  $L_2$ , measured by the more closely hatched area. The total work  $L$  produced in the whole cycle, therefore, appears as the difference  $L_1 - L_2$ .

We see, moreover, that Fig. 7a represents nothing but what is known and familiar to the mechanical engineer as an indicator diagram. As the same process can be repeated as often as desired, we can easily refer the gained work  $L$  to the second of time and can express it in horse-powers, provided we know how many times the process takes place in a second.

Steam engines, hot-air engines, gas (internal-combustion) engines, which I include under the general name of heat engines, do in fact produce diagrams or processes of the described kind; of course, in very special cases we must first investigate whether the process of the one or the other kind of engine really can be regarded as reversible, for only under this supposition do the above general propositions hold; particularly should direct application to the occurrences in internal-combustion engines be preceded by a special investigation, because here the process is connected with a chemical change, a condition which has hitherto been expressly excluded from the investigation. In applying thermodynamics to technical problems we will come back to the foregoing.



$$L = \frac{Q_1}{A} - \frac{Q_2}{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

or

$$AL = Q_1 - Q_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

and considering equation (29),

$$Q = Q_1 - Q_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

We now recognize clearly whence comes the quantity of heat  $Q$  which, in this process, was converted into the work  $L$ . It is simply the excess of the imparted heat  $Q_1$  over the abstracted heat  $Q_2$ .

If we reverse the process (Fig. 7b), then along the path  $ee_3e_2$  there will take place the supply of the quantity of heat  $Q_2$ , and along the path  $e_2e_1e$  the withdrawal of the heat  $Q_1$ ; both quantities of heat, and therefore also the quantity of heat  $Q$  (equation 32), and likewise the work  $L$  (equation 29), change their signs: in this case the withdrawn quantity of heat is larger than the supplied quantity, and the excess corresponds exactly to the quantity of heat which has been generated in this process by the external work expended.

It was shown above that, for any passage of a body from one adiabatic to another, the magnitude

$$P = \int \frac{dQ}{AS}$$

(equation 26) is a constant; if the body in our cycle first traverses one of the branches  $ee_1e_2$  or  $ee_3e_2$ , and then comes back upon the other, the magnitude of  $P$  has the same value for the forward motion as for the return motion; the only difference is a change of sign, and the sum of the two values is therefore zero.

For a cycle, and, as we must expressly add, for the "reversible cycle," there accordingly holds the relation

$$\int \frac{dQ}{AS} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

a proposition which is self-evident from our whole discussion.

The function  $S$  was so chosen at the start that the expression under the integral sign of equation (33) represented a complete



differential. Now, if we effect this integration by a change of state in which the final condition coincides with the initial one, then the integral must be equal to zero, because the integration limits are alike.

Returning once more to the consideration of Fig. 7*b*, and imagining the cycles to be conducted in the direction of the arrow, then the body, which we will call the "intermediate or mediating" body, receives the heat  $Q_1$  along the path  $ee_1e_2$ .

But the imparting of heat cannot be conceived without assuming at least another second body,  $K_1$ , which delivers said quantity of heat to the mediating body; we can also imagine a series of such bodies successively giving off heat.

Furthermore, we must assume a third body  $K_2$  (or a community of such bodies) which withdraws along the path  $e_2e_3e$  from the mediating body the quantity of heat  $Q_2$ , that is, absorbs it.

The cycle therefore includes the interaction of at least three bodies: one of them,  $K_1$ , furnishes the quantity of heat  $Q_1$ , the other,  $K_2$ , absorbs the quantity of heat  $Q_2$ , and the third, the mediating body, describes the cycle; the latter body returns to the initial condition, while the other two must necessarily experience changes of state of a certain kind. It is only when the cycle is carried out first in one direction, and then along the same paths in the reverse direction, that all three bodies return to the initial condition. But then work is neither produced nor consumed.

A glance at my graphical representation of the events in the reversible cycle of Fig. 7*b* shows that no such process is conceivable in which, with a gain or loss of work, there is not simultaneously connected a transfer of heat from a body  $K_1$  to another,  $K_2$ , or conversely.<sup>1</sup>

<sup>1</sup> Clausius in his papers speaks of "transformations" of two kinds in the reversible cycle. By "transformation of the first kind" he understands a conversion of heat into work, or, conversely, effected by the mediating body. "Transformation of the second kind" includes that transformation of heat from a body  $K_1$  to another,  $K_2$  which accompanies such a cycle.

Sadi Carnot has discussed the cycle, although only for a special case which will be more closely examined above in the text; he was led to his investigations as an engineer, by a close consideration of the occurrences in the steam engine. Later (1834) Clapeyron took up the question, and was the

## § 10. CARNOT'S CYCLE.

The propositions just developed in general fashion for the reversible cycle, under the assumption that the changes of state of the mediating body take place according to a closed curve (Fig. 7a and 7b), also hold (as is directly shown by our "graphical representation") for cases in which the work area  $L$  is bounded in parts by pressure curves of different species; of the infinite number of cases of this sort, we will now pick out one cycle whose closer investigation leads to especially important results, namely, the one whose work area is bounded by two adiabatics and two isothermals; a cycle of this kind we may designate in advance as the *Carnot cycle*.

If in Fig. 8 we draw the two adiabatics  $P_1$  and  $P_2$  and then the two isothermals  $S_1$  and  $S_2$ , we get a quadrilateral,  $a_1b_1b_2a_2$ , of curves in place of the closed curve in Fig. 7b.

If the body starts from the initial condition corresponding to point  $a_1(p_1, v_1)$ , for which  $S = S_1 = f(p_1, v_1)$ , and expands from  $a_1$  to  $b_1$ , with the corresponding supply of heat  $Q_1$ , and then, shutting off the supply of heat, expands adiabatically from  $b_1$  to  $b_2$ , then

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first to put *Carnot's* proposition in analytical form, and to also represent in graphical form the cycle with *Carnot's* assumptions, that is, the indicator diagram.

But both writers, if I may use the phraseology of *Clausius*, had in view only the "transformation of the second kind," and ascribed the production of work in heat engines solely to the transfer of heat from the body  $K_1$  (according to the designation given above in the text) to the body  $K_2$ , and assumed that here the quantities of heat were equal, that is,  $Q_1 = Q_2$ .

We must thank *Clausius's* "Abhandlungen" (1850) for pointing out what was so important for the further development of thermodynamics, namely, that the above-mentioned equality could not exist; indeed, that, according to the theorem of the equivalence of work and heat, necessarily the relation  $Q_1 > Q_2$  must obtain, and that the difference between them corresponds exactly to the work produced in the cycle.

It is what rarely occurs in science that just the most important parts of *Clapeyron's* analytical investigations were not touched by his false assumption; particularly that equation remained valid which was designated above in the text as the second fundamental equation of the mechanical theory of heat.

It might therefore be designated as *Clapeyron's* equation if, corresponding to the historical development, the first fundamental equation were named after *Clausius*.

the body can be led back to its initial state by compression along the isothermal curve  $b_2a_2$ , and by compression along the other adiabatic from  $a_2$  to  $a_1$ . In leading back along the path  $b_2a_2$ , which occurs with  $S=S_2$  constant, the quantity of heat  $Q_2$  must be withdrawn.

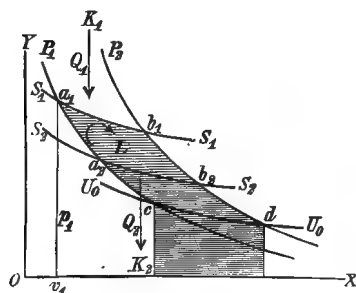


FIG. 8.

Now if we again draw an isodynamic curve  $U_0 = F(p, v) = \text{constant}$ , which cuts the adiabatic in  $c$  and  $d$ , then, as was proved, the whole hatched area of Fig. 8 represents the heat  $Q_1$  measured

in units of work, and similarly the more closely hatched area represents the heat  $Q_2$  measured in the same units; the difference of the two is again the work  $L$  produced in the cycle: here equation (30) and equation (31) likewise hold; moreover, according to equation (28), page 46, the heat weight, the entropy  $P$ , is the same for each of the two isothermal passages, and, indeed,

$$P = \frac{Q_1}{AS_1} = \frac{Q_2}{AS_2} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{IV})$$

Accordingly,  $Q_1 = APS_1$  and  $Q_2 = APS_2$ , and, therefore, from equation (30), which we here rewrite, the work produced in this cycle becomes:

$$\left. \begin{aligned} L &= \frac{Q_1}{A} - \frac{Q_2}{A}, \\ L &= P(S_1 - S_2). \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (\text{V})$$

These equations are identical, and  $P$  is determined by equation (IV).

Now the following is deserving of notice. Because  $Q_1 > Q_2$  (for the difference is the heat corresponding to work  $L$ ), we also always have  $S_1 > S_2$ , according to equation (IV). Now, although at this time nothing is known concerning the form of the equation  $S = f(p, v)$ , still we at least know that the value of the constant  $S$  in any single one of the infinite host of isothermal lines

traversing the diagram is larger, the higher the curve lies in the diagram. For each point of the plane below the curve  $S_1S_1$  (Fig. 8) we have the corresponding value of  $S$  smaller, and for every point lying above it  $S$  is greater than the constant  $S_1$  of the assumed isothermal.

The following important remark is closely connected with the foregoing.

If a body describes any cycle  $abcd$  whatever, Fig. 9, and if we draw two adiabatics  $P_1$  and  $P_2$  and two isothermals  $S_1S_1$  and  $S_2S_2$ , which touch the curve, then for every point of the cycle the corresponding value  $S$  is smaller than at the point of contact  $b$ , and greater than the value at the point of contact  $d$ .

Now if the curve  $S_1S_1$  (Fig. 9) were given as a certain upper limit, and the curve  $S_2S_2$  as a lower limit, that is, if it were impossible in the course of the cycle  $abcd$  to pass beyond the upper and lower limits ( $S_1$  and  $S_2$ ), then the area enclosed by the curve  $abcd$  would always be smaller than the area  $a_1b_1a_2$ .

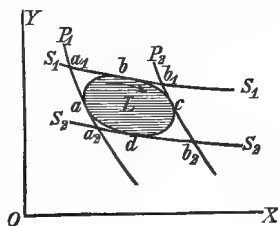


FIG. 9.

From this follows a proposition of especial importance for the theory of engines:

“Of all the cycles which can be described between two particular adiabatics and two particular isothermals, the Carnot Cycle will deliver the maximum of work  $L$ .”

Let us now return to the special consideration of the Carnot cycle with the help of Fig. 8.

Along the first isothermal, along the path  $a_1b_1$ , the mediating body receives the heat  $Q_1$ , which we will suppose to come from a body  $K_1$ , which, during the course  $a_1b_1$ , stands in a certain mutual relation to the mediating body,—for example, is in contact with it; but to this body  $K_1$  must evidently be ascribed a particular property, namely, that it will, as the case may be, successively impart heat to, or withdraw heat from, the mediating body in such measure that the function  $S$  will be maintained at the constant value  $S_1$ . The body  $K_1$  may therefore be designated as “body of the state  $S_1$ ”; for like reasons we must also imagine

a second "body of state  $S_2$ ," which will affect the withdrawal of heat along the isothermal  $S_2S_2$  on the path  $b_2a_2$ , or similarly affect the imparting of heat in the reversed path  $a_2b_2$ . Now we will for the present dismiss the consideration whether bodies with the given properties really exist or not; the assumptions made do not alter the general character of the considerations; we can even say that it is undoubtedly correct that an exchange of heat would take place between the bodies  $K_1$  and  $K_2$  if they were brought into immediate contact; the only doubt remaining in the matter would be as to the direction in which the heat exchange would take place,—whether from  $K_1$  to  $K_2$  or in the opposite direction; at any rate, there would be no production of work in such a direct exchange of heat.

We can now say briefly that in the Carnot cycle the heat weight  $P$  is transferred from the body  $K_1$  of the state  $S_1$  to the body  $K_2$  of the state  $S_2$ , and that thus the work  $L = P(S_1 - S_2)$  is produced, and that this work, having a particular heat weight  $P$ , is a maximum as compared with all the other possible cycles which can be described between the limits  $S_1$  and  $S_2$ . During the reversal of the cycle an equal amount of work is consumed and the heat weight is inversely transferred from body  $K_2$  to body  $K_1$ .

## § 11. PHYSICAL SIGNIFICANCE OF THE FUNCTION $S$ .

Hitherto all propositions established in the foregoing have proceeded from the assumption of a single fundamental principle, namely, the equivalence of heat and work. But further progress now demands the setting up of another or second fundamental principle, in order to briefly determine the form and significance of the different functions thus far introduced. If we succeed in doing this for at least one of them,—for example, for the function  $S = f(p, v)$ ,—then we know, from what has already been said, that we have the means given in the fundamental equations deduced above of immediately expressing all the remaining functions.

Before going into the further developments indicated, it will be useful to compare the propositions concerning the cycles, par-

ticularly those concerning the Carnot cycle, with the analogous principles of Mechanics.

Let us imagine three horizontal planes  $A$ ,  $B$ , and  $C$  lying over one another. The uppermost plane,  $A$  (Fig. 10), lies at the height  $H_1$ , and the second,  $B$ , at the height  $H_2$  over the lowest plane,  $C$ ; the lowest plane therefore lies at the zero point, from which the heights are measured upward; furthermore, if we imagine there is at our disposal in the uppermost plane a body of the weight  $G$ , and that we can let it sink slowly and uniformly to the lowest plane, then there will be at our disposal in this body a work which may be designated by  $W_1$ , which is easily determined by the relation,

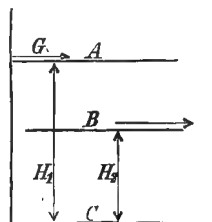


FIG. 10.

$$W_1 = GH_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

The value  $W_1$  is what is designated in Mechanics as "energy of position," or as "potential energy due to the action of gravity." If the same weight  $G$  exists on the middle level  $B$ , then there will be produced, during its slow, uniform sinking to the lowest level, the work

$$W_2 = GH_2; \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

finally, the work  $L$ , which is produced when the body sinks in like manner from  $A$  to  $B$ , is

$$L = G(H_1 - H_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

From equations (34) and (35) follows

$$G = \frac{W_1}{H_1} = \frac{W_2}{H_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (IVa)$$

and substitution in equation (36), which we will write again, gives

$$\left. \begin{aligned} L &= W_1 - W_2, \\ L &= G(H_1 - H_2). \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad . \quad (Va)$$

If we imagine a body of weight  $G$  to be slid along in the plane  $A$ , then this corresponds to a "supply" of the work  $W_1$ , and

the body after it has descended to the level  $B$ , doing work in the manner indicated, must be there delivered, and this will correspond to a "withdrawal" of the work  $W_2$ ; the difference between the furnished work  $W_1$  and the led-away work  $W_2$  (which for our purposes can be considered as work withdrawn) is equal, according to equation (Va), to the work  $L$  produced. But the cycle is also reversible, and if the body is led to the lower level  $B$  and then lifted slowly and uniformly into the upper level  $A$ , then the furnished work  $W_2$  at  $B$  is smaller than the delivered  $W_1$  at  $A$ ; the work  $L$  has been expended in lifting and corresponds exactly to the difference  $W_1 - W_2$ .

If we again imagine a cycle to be described in the first direction, then, under the assumptions made, the work  $L$ , produced in passing from  $A$  to  $B$ , is a maximum, because uniform sinking was assumed; for if the sinking were not uniform, that is, were accelerated, occurring with increasing velocity, then the work produced would be smaller, indeed this work might even be zero when the body of weight  $G$  simply falls from  $A$  to  $B$ ; in this case there dwells in the body at the lower level the whole initial work  $W_1$ , but the difference  $W_1 - W_2$  exists in the form of living force, of kinetic energy. For the purpose of technical study, which, to be sure, is the main purpose of the present treatise, it is convenient to regard the body  $G$  as a liquid; if the level  $A$  is an infinitely broad and extremely shallow reservoir, and likewise the level  $B$ ,<sup>1</sup> and if  $G$  is the weight of a quantity of water which sinks in a particular interval, for example in one second, then the process described in the foregoing will appear as the one carried out by the hydraulic motors, water wheels, turbines, and water-pressure engines; the reversal of the process would then correspond to hydraulic hoists, scoop wheels, centrifugal pumps, and cylindrical pumps.

The choice of the lower level  $C$  is still perfectly arbitrary; in

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<sup>1</sup> This assumption is always made in the investigation of hydraulic motors; if we proceeded more exactly and assumed finite values for the breadth and depth of the supply and discharge conduits, then we ought to take for the difference of heights  $H_1 - H_2$  the distance apart of the centers of gravity of the two conduit cross-sections; we should also assume that the water flows at all points with the same velocity and does the same in the discharge conduit.

considering hydraulic motors we may imagine it to be at the level of the sea.

If we compare the formulas and principles in the foregoing with those which were given for the Carnot cycle (§ 10, p. 53), with the help of Fig. 8, then the complete analogy will appear; and where we there spoke of the heat quantities  $Q_1$  and  $Q_2$ , measured in units of work, we here have the quantities of work  $W_1$  and  $W_2$ ; and where we there expressed the values of function  $S$  by  $S_1$  and  $S_2$ , we here have the heights  $H_1$  and  $H_2$ . Equations (IVa) and (IV) are in structure and meaning like (Va) and (V).

Function  $S$  can therefore be regarded as a linear quantity, the height of a level over a certain zero point, and the analogy between the two kinds of occurrences is just what incited us to designate the value  $P$  given by equation (26), page 44, as "heat weight," which designation can even be applied to the differential

$$dP = \frac{dQ}{AS}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

in this case the work produced in the Carnot cycle between the limits  $S_1$  and  $S_2$  is

$$dL = (S_1 - S_2)dP. \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

On the other hand, if we imagine the uniform sinking of a body of infinitesimal weight,  $dG$ , possessing at the height  $H$  the work  $dW = HdG$ , we have

$$dG = \frac{dW}{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (37a)$$

and the work produced in falling from  $H_1$  to  $H_2$  is

$$dL = (H_1 - H_2)dG. \quad . \quad . \quad . \quad . \quad . \quad . \quad (38a)$$

The last two equations and the cycle underlying them could easily be extended in such a way as to bring out the general propositions given for any cycle.

But for the important questions before us it will suffice to keep in view the simple Carnot cycle.



Just as the consideration of the events based on Fig. 10 reproduced occurrences in hydraulic motors and their inversions, the hydraulic hoists, so here the question arises whether a closer examination of the occurrences in heat engines and their inversions could not be utilized for the events in the Carnot cycle and lead to further information.

If we think especially of the steam engine, then in fact a transfer of heat from the boiler to the condenser does accompany the production of work in a steam cylinder; heat is imparted to the boiler, and cooling takes place in the cylinder, that is, heat is withdrawn. But here the heat supply takes place at high temperature, and the heat withdrawal at lower temperature.

We can therefore say that in the steam engine we have before us a case of work production occurring simultaneously with a passage of heat of higher temperature to heat of lower temperature. The inverse process occurs in refrigerating engines, engines which serve for the production of cold; to run these engines work is expended and the imparting of heat in the evaporator takes place at the lower temperature, the withdrawal of heat (in the condenser) at the higher temperature.

Here, therefore, we really have to do with a cycle described by engines which work in the one or the other direction according to the need of the moment, that is, we have to do with a cycle that is reversible. In the boiler, as in the condenser, the temperatures are maintained at constant height during the running.

But now the foregoing considerations show that in the described cycle a new element comes into play which did not exist in our former discussions, or, to speak more exactly, existed there in disguised form, namely, temperature.

Let us designate, according to Celsius, the temperature by  $t$ , whose zero is the freezing-point of water, and whose 100 is the boiling-point of water, both corresponding to the mean barometric height of 760 mm. mercury; then it is a question whether all the discussed peculiarities of the Carnot cycle and of the properties belonging to the function  $S$  will really correspond with experience if we assume that in this cycle the expansion of the body takes place

along the path  $a_1b_1$  (Fig. 11) at constant temperature  $t_1$ , and that the compression takes place along the path  $b_2a_2$  at the lower temperature  $t_2$ . In this case the body  $K_1$  of the state  $S_1$  appears to be one which maintains at constant temperature the mediating body during its expansion. This will occur when  $K_1$  itself is so large (strictly speaking, infinitely large) that its grant of heat does not cause any noticeable change in its own temperature. Likewise the body  $K_2$ , which has to maintain along the path  $b_2a_2$  the mediating body at the constant temperature  $t_2$ , must be assumed to be very great and to possess the temperature  $t_2$ . Bodies of this sort do exist, and consequently the Carnot cycle seems to be drawn within the realm of possibility, even if we disregard the experience of heat engines.

Accompanying the production of work by means of the Carnot cycle, there is a transfer of heat from the body  $K_1$  of the higher temperature  $t_1$  to a body  $K_2$  of the lower temperature  $t_2$ , which is what actually happens in heat engines and was described when considering steam engines.

Furthermore, experience shows that a direct transfer of heat from  $K_1$  to  $K_2$  without production of work is possible, a case which we just compared (in Fig. 10) with the falling of a weight from a higher to a lower level. We only need to bring the two bodies of different temperatures  $t_1$  and  $t_2$  into contact with each other, in which case heat of its own accord flows from the warmer to the colder body, a procedure known under the name of **heat conduction**.

But never has there been observed during the direct contact of two bodies  $K_1$  and  $K_2$  a transfer of heat in the opposite direction, that is, a flow from a body of lower temperature to one of higher temperature; such a transfer, according to the reversal of the Carnot cycle (Fig. 11), is only possible with the simultaneous performance of external work, and without it could only be com-

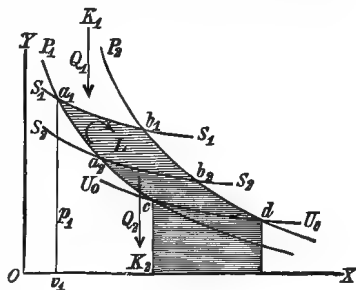


FIG. 11.

pared with the phenomenon of a weight rising uniformly without expenditure of work, that is, alone and unaided, from a lower level to a higher one.

From all the foregoing consideration of the function  $S=f(p, v)$  we conclude that the temperature is constant when the change of state of a body takes place with constant value of  $S$ . Therefore we must also regard  $S$  as a function of the temperature  $t$  alone. Accordingly we have the relation

$$S=\phi(t),$$

and an expansion or compression according to the curve  $S=\text{constant}$  appears as a change of state at constant temperature; for this reason this curve was designated from the beginning as the isothermal curve.

## § 12. TRANSFORMATION OF FUNDAMENTAL EQUATIONS.

As  $S$  has been recognized as a function of the temperature  $t$ , we have the relation

$$dS=\frac{dS}{dt}dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Now it has long been recognized in Physics that the temperature  $t$  of a body is completely determined by the pressure  $p$  and the volume  $v$ . The analytical relation existing between  $t$ ,  $p$ , and  $v$  for a particular body, and assumed to be derived from physical considerations, is called (according to Bauschinger) the "equation of condition" of the body in question. This equation of condition appears to be different for different forms of the body, and is not known for all kinds of bodies; at the present time it is only known for gases, and, as will be discussed later, for vapors in certain conditions, but not for solid and liquid bodies. But the equation of condition when known invariably gives the relation

$$dt=\frac{\partial t}{\partial p}dp+\frac{\partial t}{\partial v}dv,$$

and if we use this in equation (39) we get

$$dS = \frac{dS}{dt} \left( \frac{\partial t}{\partial p} dp + \frac{\partial t}{\partial v} dv \right). \quad . \quad . \quad . \quad . \quad . \quad (40)$$

If we compare this formula with the earlier one given under (19), page 35, there follows

$$\frac{\partial S}{\partial p} = \frac{dS}{dt} \cdot \frac{\partial t}{\partial p} \quad \text{and} \quad \frac{\partial S}{\partial v} = \frac{dS}{dt} \cdot \frac{\partial t}{\partial v} \quad . \quad . \quad . \quad . \quad (41)$$

But now the second fundamental equation of the mechanical theory of heat (II, page 34) was found to be

$$S = Y \frac{\partial S}{\partial p} - X \frac{\partial S}{\partial v},$$

and if we here utilize equation (41) we get

$$\frac{S}{\frac{dS}{dt}} = Y \frac{\partial t}{\partial p} - X \frac{\partial t}{\partial v}.$$

As  $S$  is only a function of  $t$ , the expression in the left member is also only a function of  $t$ , and we can therefore put

$$T = \frac{S}{\frac{dS}{dt}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

and this new temperature function  $T$ , whose special form is still to be determined, we will, till this form is established, call the Carnot Function. It stands in a simple relation to the function designated by  $S$ , for from equation (42) follows

$$\frac{dS}{S} = \frac{dt}{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

and therefore

$$\log_e S = \int \frac{dt}{T} + C, \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where  $C$  represents an integration constant. As soon, therefore, as the form of Carnot's temperature function is recognized,—and we will derive it below from physical principles,—so soon will equation (44) determine the magnitude  $S$  as a function of the temperature  $t$ .

For the purpose of the following investigations, and in order to easily refer to the principal results of all the foregoing investigations, we will here collect the principal formulas. The first fundamental equation (I), p. 32, is repeated unchanged in (Ia); on the other hand, the second fundamental equation (II), after utilizing the equation preceding equation (42), takes the form shown in (IIa):

$$\frac{\partial Y}{\partial p} - \frac{\partial X}{\partial v} = 1, \quad . . . . . \text{(Ia)}$$

$$Y \frac{\partial t}{\partial p} - X \frac{\partial t}{\partial v} = T. \quad . . . . . \text{(IIa)}^1$$

On the other hand, of equations (III), page 36, only the second and third change their form when equations (41) and (43) are utilized, a transformation which is easily followed, and we can therefore write

$$\left. \begin{aligned} dQ &= A[X dp + Y dv] \\ &= \frac{A}{\frac{\partial t}{\partial p}} [X dt + T dv] \\ &= \frac{A}{\frac{\partial t}{\partial v}} [Y dt - T dp] \\ &= A[dU + p dv] \\ &= AS dP \end{aligned} \right\} . . . . . \text{(IIIa)}$$

and from this grouping of five identical equations we will always pick out that one which most readily leads to the solution of the particular problem.

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<sup>1</sup> Clapeyron gave the second fundamental equation exactly in the form in which it is represented by (IIa), only he used the letter  $C$  to designate the Carnot Function  $T$ .

### § 13. UNIVERSAL SIGNIFICANCE OF THE CARNOT FUNCTION.

In the above investigation of cycles, particularly of the Carnot cycle, only one body was mentioned, and its change of state considered. When the result was ascertained that the two functions  $S$  and  $T$  could be regarded as temperature functions of a particular kind, then evidently this result could for the time being hold only for the body in question describing the Carnot cycle.

But it can now be shown, and this is the purpose of the following discussion, that the form of this function must be the same for bodies of every kind, whether they exist in gaseous, liquid, or solid condition. If the proof is furnished for one of the two functions, then it will also hold for the other function on account of relation (44).

If we assume two different bodies  $A$  and  $B$ , and describe with each a Carnot cycle between two isothermals corresponding to the same limiting temperatures  $t_1$  and  $t_2$ , and indeed in such a way (as is always possible by a suitable choice of the corresponding adiabatics) that the work performed, or the work  $L$  expended during the reversal of the cycle, is the same, then we can utilize in both cases the bodies  $K_1$  and  $K_2$  for the supply and withdrawal of heat.

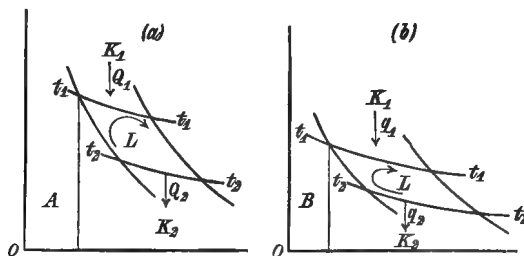


FIG. 12.

If in Fig. 12a we describe the indicated cycle process in the direction of the arrow with the first body  $A$ , then the body  $K_1$  will furnish the quantity of heat  $Q_1$  and the body  $K_2$  will absorb

the quantity of heat  $Q_2$ , and the work  $L$  produced will bear, to the given quantities of heat, the relation

$$AL = Q_1 - Q_2.$$

On the other hand, if we describe the same cycle in the same direction with the second body  $B$  (Fig. 12*b*), we may assume that the body  $K_1$  will supply to  $B$  the quantity of heat  $q_1$  during isothermal expansion, and the body  $K_2$  will absorb during the isothermal compression the quantity of heat  $q_2$ . As the work here must also be equal to  $L$  we have the formula

$$AL = q_1 - q_2.$$

From this follows, by a combination of the two formulas:

$$Q_1 - Q_2 = q_1 - q_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

From the equating of the differences, however, it does not necessarily follow that the equations  $Q_1 = q_1$  and  $Q_2 = q_2$  must be true; rather the only permissible conclusion is that we have the relations

$$\left. \begin{aligned} q_1 &= Q_1 + Q_0, \\ q_2 &= Q_2 + Q_0, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

where  $Q_0$  represents a positive or negative quantity of heat.

Let us assume that  $Q_0$  is positive, and let us describe the cycle with the body  $A$  in the direction of the given arrow (Fig. 12*a*), then the body  $K_1$  will furnish the quantity of heat  $Q_1$ ; now utilizing the same bodies  $K_1$  and  $K_2$  with the body  $B$ , let us conduct the cycle (Fig. 12*b*) in the direction opposed to the arrows. Then the body  $K_1$  at the upper temperature  $t_1$  will absorb the quantity of heat  $q_1 = Q_1 + Q_0$ , while it only gave out during the first cycle the quantity of heat  $Q_1$ . Both mediating bodies  $A$  and  $B$  are thus brought back to their initial condition; during the first cycle the work  $L$  was produced, while during the second cycle an equal quantity of work was consumed. The sole result after this double cycle is that the body  $K_2$  of the

lower temperature  $t_2$  possesses an amount of heat less by  $Q_0$  than formerly, and the body  $K_1$  of the higher temperature an amount greater by  $Q_0$ ; it would therefore appear as if the quantity of heat  $Q_0$  had simply of itself been transferred from the body  $K_2$  of lower temperature  $t_2$  to a body  $K_1$  of the higher temperature  $t_1$ .

The same result is produced when we take  $Q_0$  in equations (46) as negative; in this case we would use

$$\begin{aligned} Q_1 &= q_1 + Q_0, \\ Q_2 &= q_2 + Q_0, \end{aligned}$$

and would get the same result as before, provided the second body  $B$  first described the cycle (Fig. 12*b*) in the direction given by the arrow, and that then the cycle course were completed with the first body  $A$  in the direction opposed to the arrow.

These considerations led Clausius to a simple proposition which has been universally accepted as the second fundamental law, namely:

“Heat cannot of itself pass from a colder to a hotter body”; it has been placed alongside of the first law (that heat and work are equivalent) of the mechanical theory of heat. It follows that in the foregoing developments the introduced quantity of heat  $Q_0$  can have neither a positive nor a negative value, but must be equal to zero.

Equation (46) therefore becomes

$$\left. \begin{aligned} Q_1 &= q_1, \\ Q_2 &= q_2. \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (47)$$

In the two cycles represented by Figs. 12*a* and 12*b* the body  $K_1$  therefore receives back the same quantity of heat  $Q_1$  during the reversal of the cycle which it formerly supplied, and the body  $K_2$  gives out again the same quantity of heat  $Q_2$  which it previously received, no matter which body acted mediately in the first forward direct cycle or in the second return reversible cycle.

The importance of this proposition justifies us in returning for a moment to the analogous case in Mechanics treated in § 11.



If we assume that a turbine consumes  $G$  kg [lb.] of water per second with a fall  $H_1 - H_2$  (see Fig. 10, p. 55), then, neglecting the losses of work, its corresponding work will be  $G(H_1 - H_2)$ . Now if this turbine drives a centrifugal pump, and we here also neglect the losses of work, then the same quantity of water  $G$  can be brought back to the original level  $H_1$ ; and if the original quantity of work supplied at this level is  $W_1 = GH_1$ , then this also will be brought back again. Now if we try to conceive of a machinal arrangement which would bring a larger quantity of work  $W_1 + W_0$  into the upper plane, then this would be equivalent to the assumption that the weight

$$G_0 = \frac{W_0}{H_1}$$

could be brought from a lower to a higher level without the expenditure of work. But since this weight  $G_0$  could be allowed to sink while at work (for example, in a second turbine), this arrangement of the two turbines with a centrifugal pump would constitute a case of perpetual motion, the impossibility of which was long ago demonstrated.

But what is true of the hydraulic motors is also true of the heat engines; if we had two such engines describing the Carnot cycle, given in Figs. 12*a* and 12*b*, both working between the same temperature limits, and the one engine running through the forward cycle and the other through the reverse cycle, and if, moreover, in the former the amount of work produced was numerically equal to the amount of work consumed in the latter, then it would be impossible for the quantity of heat supplied to the body  $K_1$  to be greater than the quantity of heat which it gave out during the first cycle; for if it were greater, and the excess were represented by  $Q_0$ , then this quantity of heat existing at the upper-temperature level could be utilized and describe a third Carnot cycle by means of a third engine.

In reality Clausius's principle amounts to saying that in a mechanical sense no combination of heat engines is conceivable which will bring about perpetual motion.

Now let us return to the discussion of the main question. Con-

sideration of the two cycles given in Figs. 12*a* and 12*b* has led to the result that, assuming the same temperature limits and equal quantities of work, the relations

$$Q_1 = q_1$$

$$Q_2 = q_2$$

must be true, and it consequently follows that

$$\frac{Q_1}{Q_2} = \frac{q_1}{q_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

But still it does not follow that the function  $S = \Psi(t)$ , page 60, must have the same form for the two bodies  $A$  and  $B$ ; to be sure, the two isothermal curves for the body  $A$  (Fig. 12*a*) certainly have a different course than for the body  $B$  when we consider the connection of  $S$  with  $p$  and  $v$ , and we may here say that this difference really exists: because of the connection of the value  $S$  with the temperature a further discussion of the question is necessary.

If for the body  $A$  we designate the temperature function by  $S$ , as hitherto, and on the other hand for the body  $B$  by  $s$ , and thus distinguish another form of the function, then, according to equation (28), we have the relation,

$$\frac{Q_1}{AS_1} = \frac{Q_2}{AS_2} \quad \text{or} \quad \frac{Q_1}{Q_2} = \frac{S_1}{S_2}.$$

For the other cycle there is likewise,

$$\frac{q_1}{As_1} = \frac{q_2}{As_2} \quad \text{or} \quad \frac{q_1}{q_2} = \frac{s_1}{s_2}.$$

According to equation (48) there immediately follows

$$\frac{s_1}{s_2} = \frac{S_1}{S_2}.$$

If we subtract unity from both sides, we can also write

$$\frac{s_1 - s_2}{s_2} = \frac{S_1 - S_2}{S_2}.$$

As a consequence, if we suppose the two cycles in Fig. 12*a* and Fig. 12*b* to work between the limiting temperatures  $t_2 = t$  and  $t_1 = t + dt$ , we have

$$\frac{ds}{s} = \frac{dS}{S},$$

and therefore, by integration,

$$s = kS, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

where the factor  $k$  is a constant. This proves, first of all, that the temperature factor  $S$  for the one body  $A$  differs in value from that of the other body  $B$  only by this factor. But in § 5, p. 33, the function  $S$  was introduced into equation (15) as an integrating factor, and, in the accompanying remark there made, it was emphasized and proved that we could substitute for this function the value  $kS$  without altering at all any one of the following conclusions; consequently the factor  $k$  is perfectly arbitrary, and therefore may also be placed equal to unity. But independently of this we find, when we differentiate equation (49) with respect to temperature,

$$\frac{ds}{dt} = k \frac{dS}{dt}.$$

If we divide equation (49) by this one and at the same time make use of equation (42), p. 61, we get

$$T = \frac{s}{\frac{ds}{dt}} = \frac{S}{\frac{dS}{dt}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

and this magnitude, according to equation (42), was designated as the Carnot temperature function  $T$ .

From this follows the important result, that the Carnot function must not only have the same form for all bodies of nature, but must also, at any particular temperature, have *one and the same numerical value* for all bodies without exception.

## § 14. TRANSFORMATION OF REVERSIBLE PRESSURE CURVES AND OF INDICATOR DIAGRAMS.

If a body starting from the initial condition  $(p_1, v_1)$ , Fig. 13a, passes to the final condition  $(p_2, v_2)$ , traversing the prescribed pressure curve  $acb$  while receiving the quantity of heat  $Q$ , there will correspond to the curve point  $c$ , having the coördinates  $p$  and  $v$ , a perfectly definite value of the function  $S$  and of its temperature  $t$ , for we will continue to assume as known the two relations,

$$S = f(p, v) \quad \text{and} \quad S = \psi(t).$$

Likewise the function

$$P = \int \frac{dQ}{AS} = \phi(p, v)$$

has for this point  $c$  a value which can be determined from this given equation.

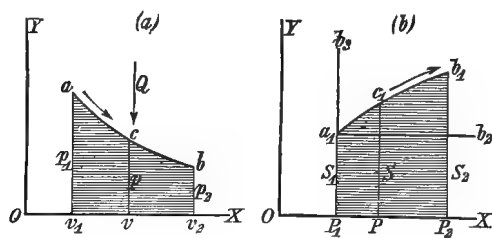


FIG. 13.

If we now lay off from  $O$ , in Fig. 13b, the value  $P$  as abscissa  $OP$  and the value  $S$  as its corresponding ordinate, we get point  $c_1$ , which we will call the transfer (copy) of the point  $c$  of the pressure curve.

In this way every point of the pressure curve can be reproduced as soon as we know its course, and consequently we get in Fig. 13b a curve  $a_1c_1b_1$  which may be designated as the transformation of the pressure curve  $acb$ .

If in a special case  $acb$  is the isothermal curve, for which we know, from what has preceded, that the temperature  $t$  and its corresponding value  $S=S_1$  are constant, it will follow that the transformation of the isothermal will be a straight line  $a_1b_2$  lying parallel to the axis of abscissas  $OX$ .

On the other hand, if the pressure curve  $acb$  is an adiabatic, then we know, from the discussion of Fig. 5, § 8, and from equation (23), p. 39, that the function  $P=P_1$  is a constant; therefore the transformation  $a_1b_3$  of the adiabatic curve passing through the point  $a$  is a straight line lying parallel to the axis of ordinates.

Now if we again return to the general case in Fig. 13b, and allow the distance  $P$  to increase by the amount  $dP$ , then the area of the strip standing on  $dP$  will be  $S dP$ ; consequently from the original relation

$$dP = \frac{dQ}{AS}$$

there follows also

$$\frac{dQ}{A} = S dP,$$

and therefore the area  $a_1b_1P_2P_1$  (hatched in the figure) lying under the transformed curve  $a_1c_1b_1$  represents nothing but

$$\frac{Q}{A} = \int S dP,$$

i.e., the quantity of heat  $Q$ , measured in units of work, which must be imparted to the body during its changes of state along the path  $acb$ ; the area  $abv_2v_1$  (Fig. 13a) under the latter curve measures the external work thus produced at the same time.

Besides the graphical determination of the heat quantity  $Q$ , given in connection with Fig. 4, § 7, p. 41, there follows from the above a second graphical method for the same purpose, and one free from the defects there emphasized.

We must not overlook the fact that both methods are only true for reversible operations. If Fig. 13a refers to compression, the reversal of the operation before assumed, then the direction of the arrow in Fig. 13b will also be reversed, and the quantity of heat will be negative, that is, will be heat withdrawn, and the hatched area in Fig. 13a will represent the work consumed. It is self-evident that heat withdrawal may exist during expansion, a case which would at once manifest itself in the transformation, by the distance  $OP_2$  being less than  $OP_1$ .

The propositions here developed, of course, also hold when the given pressure curve is a closed curve, therefore also when we are dealing with a reversible cycle.

If Fig. 14a represents a certain indicator diagram, we know from earlier discussions that the area inclosed by the curve represents the work produced in this cycle. The transformation (Fig. 14b), constructed in the indicated manner, then leads directly to a closed curve, and if we draw the two end-ordinates,  $P_1a_1$  and  $P_2b_1$ , touching the closed curve at the points  $a_1$  and  $b_1$ , the

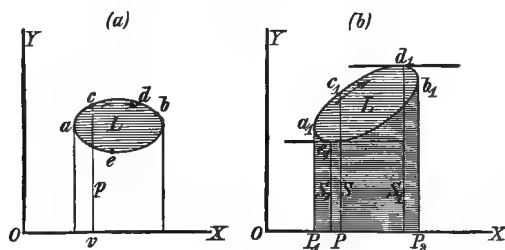


FIG. 14.

whole hatched area inclosed by the upper part  $a_1d_1b_1$  of the curve and by the end-ordinates will represent the quantity of heat  $Q_1$  (measured in units of work, that is,  $Q_1:A$ ) which must be supplied with this cycle; the area inclosed by these end-ordinates and the lower part  $a_1e_1b$  of the curve (area closely hatched in figure) will give in like manner the quantity of heat  $Q_2$  to be with-

drawn, also measured in units of work. From equation (31), namely,

$$L = \frac{Q_1 - Q_2}{A},$$

it follows that the widely hatched area of Fig. 14*b* likewise represents the work  $L$  produced in this cycle; in other words, the transformation of an indicator diagram gives the (indicated) work  $L$ , but at the same time it furnishes the means of determining the supplied and withdrawn quantities of heat  $Q_1$  and  $Q_2$ ; and this can be accomplished in a simple way by area determinations, which can be undertaken with the planimeter, as is very generally done at the present time in measuring indicator cards for the work  $L$ .

Moreover, from the position of the two contact points  $a_1$  and  $b_1$  (Fig. 14*b*), we can, by working backwards, determine the corresponding points  $a$  and  $b$  (of the indicator diagram, Fig. 14*a*), between which the heat supply and the heat withdrawal can occur.

Furthermore, if we draw in Fig. 14*b* two horizontal lines which touch the closed curve at the points  $d_1$  and  $e_1$ , these points will correspond to the greatest and least values  $S_1$  and  $S_2$  of the function  $S$ , and, working backward from this, we can likewise determine the highest and lowest temperatures  $t_1$  and  $t_2$  occurring in this cycle; the points  $d$  and  $e$  in the indicator diagram, corresponding to the points  $d_1$  and  $e_1$ , can also be easily determined.

If in the transformation several horizontal or vertical lines occur, then this is a sign that in the cycle given by the indicator diagram there respectively exist isothermal or adiabatic expansion or compression for the corresponding distances.

The transformation of the Carnot cycle (Figs. 15*a* and 15*b*) is very simple according to this method. Two isothermals,  $ab$  and  $cd$ , appear in the transformation as the horizontal lines  $a_1b_1$  and  $c_1d_1$ , and two adiabatics,  $ac$  and  $bd$ , appear as vertical lines  $a_1c_1$  and  $b_1d_1$ . The ordinate  $P_1a_1 = P_2b_1$  represents  $S_1$ , and likewise  $P_1c_1 = P_2d_1$  represents the value  $S_2$ , corresponding to the upper and lower limits of temperature  $t_1$  and  $t_2$ ; if in addition we desig-

nate the distance  $P_1P_2$  by  $P$ , there follows, from the given significance of the individual areas, the supplied quantity of heat  $Q_1$  and also the withdrawn heat  $Q_2$  by means of the formulas

$$\frac{Q_1}{A} = PS_1 \quad \text{and} \quad \frac{Q_2}{A} = PS_2,$$

and the work produced is

$$L = P(S_1 - S_2),$$

just as was explained some time ago.

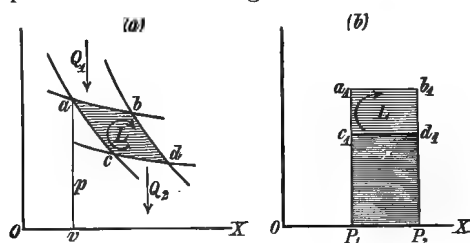


FIG. 15.

We recognize from this that a large part, in fact the most important part of thermodynamic problems, so far as they are technical, are solved as soon as we know the form of the two functions

$$S = f(p, v) = \phi(t) \quad \text{and} \quad P = \phi(p, v).$$

Future investigations will show that these functions can be determined and fixed for the very bodies (gases and vapors) which are technically most important; and therefore the method developed in the foregoing furnishes a way of solving graphically the problems of thermodynamics, and moreover provides us with an important and considerable extension in the utilization of indicator diagrams.

But we must not overlook the fact that the propositions here developed are only true under the explicit assumption that the whole cycle is reversible. Our actually built heat engines, from which we can easily take indicator diagrams, by no means describe such reversible cycles. Later investigations will show that certain portions of the indicator curve are not reversible, so that the established propositions cannot be applied to



them without modification. For the present the given graphical method <sup>1</sup> must be regarded as merely a simple help in presenting to the eye a clear and general picture of propositions concerning the reversible cycle; in attempting to employ it in technical investigations, for example in the further utilization of indicator diagrams of the steam engine, air engine, etc., for the reasons given, we encounter difficulties which can only be overcome by a further investigation of non-reversible cycles.

The aforesaid transformation of a closed curve, and therefore of an "indicator diagram," has recently and commonly been designated as "entropy diagram" and "heat diagram."

## § 15. NON-REVERSIBLE OPERATIONS.

In all the investigations hitherto made, it has been assumed that, during the change of a body from a certain initial condition ( $p_1, v_1$ ) to the final condition ( $p_2, v_2$ ), accompanied by a supply or withdrawal of heat, the external pressure is constantly maintained equal to the body tension, and in such a case the opera-

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<sup>1</sup> The first to follow out the thought of laying off the heat weight, the entropy  $P$  as abscissa and the corresponding value of  $S$  as ordinate, was Belpaire (Bull. de l'acad. roy. de Belg., 1872, Vol. 34, p. 509); he represented especially the Carnot cycle, using for  $P$  and  $S$  the formulas which are still to be established in this treatise. Prof. Linde went into the question more thoroughly in his treatise, "Theorie der Kälteerzeugungsmaschinen, graphische Darstellung der Leistungsverhältnisse derselben" (Verhandlungen des Vereins zur Beförderung des Gewerbelebens, 1875, p. 365). Further use of the method was then made by Prof. Schröter in his work "Ueber die Anwendung von Regeneratoren bei Heissluftmaschinen" (Zeitschrift des Vereins deutscher Ingenieure, 1883, Vol. 27, page 449); and recently Prof. Hermann investigated the steam-engine cycle under the, to be sure, tacit assumption that this cycle is reversible in all its parts, which is by no means the case. See "Zur graphischen Behandlung der mechanischen Wärmetheorie" (Zeitschrift des Vereins deutscher Ingenieure, 1884, Vol. 28).

Moreover, J. W. Gibbs called attention to similar graphical representations ("On Graphical Methods in the Thermodynamics of Fluids," "On Representation by Surfaces of the Thermodynamic Properties of Substances." Trans. Connecticut Academy, Vol. II, 1873). Gibbs's consideration of a curved surface possessing as coördinates the magnitudes  $P$ ,  $U$ , and  $v$  proved very fruitful for general investigation. ("Thermodynamische Studien." Translated by Ostwald, Leipsic, 1892.)

tion can be reversed, i.e., it is called a reversible one. If we now drop the assumption of the equality of the two pressures the investigations take a wider range, but in so doing a series of propositions, developed above, fail.

There is now no difficulty in setting up corresponding equations for the non-reversible operation.

If the unit of weight of a body is given by the volume  $v_1$ , and the pressure  $p_1$ , say, represented by the point  $a_1$  in Fig. 16, then for the condition of equilibrium and rest at first assumed we know the corresponding value  $U_1 = F(p_1, v_1)$ , the inner work or energy.

Now, if the external pressure is suddenly brought to the smaller value  $p_1'$  the body will expand, and, if the variability of the

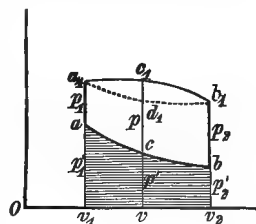


FIG. 16.

external pressure is given by the curve  $acb$ , then the area enclosed by this curve (hatched in figure) represents the external work  $L$  performed during the expansion from  $v_1$  to  $v_2$ .

At the instant at which the attainment of the final volume  $v_2$  stops all further expansion, and also during the whole course of the transition, there is evidently within the body a disturbance of equilibrium which manifests itself, for example, in gases and vapors by visible stormy motion. But after stoppage of the expansion the condition of equilibrium and of rest will gradually be reestablished, and this will evidently be accompanied by a rise of pressure from  $p_2'$  to  $p_2$ . The final condition of equilibrium at which the external pressure is identical with the internal pressure  $p_2$  will, therefore, be determined by the point  $b_1$  (Fig. 16), and the corresponding inner work by the formula  $U_2 = F(p_2, v_2)$ .

We must at once understand that we cannot return to the initial condition by the path  $bca$  simply and solely by reducing the pressure from  $p_2$  to  $p_2'$ , and that therefore such a simple reversal of the operation is not possible here.

If during the whole procedure the body receives from the outside a quantity of heat  $Q$ , then here also we have the equation

$$Q = A(U_2 - U_1 + L), \quad . . . . . (51)$$

but then the values  $U_1$  and  $U_2$  correspond to the condition of equilibrium  $a_1$  and  $b_1$ . If the expansion had been stopped earlier at the volume  $v$  (Fig. 16), then during the transition to the condition of equilibrium the pressure would have risen from  $p'$  to  $p$ , and the inner work  $U = F(p, v)$  would correspond to the point  $c_1(p, v)$ . We see from this that there arises a second curve  $a_1c_1b_1$  beside the curve  $acb$  of the external pressure. I will call the former curve the "curve of equilibrium" and the other the "curve of working pressure"; in the non-reversible operation the two curves are distinct, but are identical for the reversible procedure.

If the operation is stopped at volume  $v$ , let  $Q'$  designate the quantity of heat supplied along the path  $ac$ , and  $L'$  the work represented by the area  $v_1acv$ ; then

$$Q' = A(U - U_1 + L'). \quad . \quad . \quad . \quad . \quad . \quad (52)$$

If the operation is stopped at the volume  $v + dv$ ,

$$Q' + dQ' = A(U + dU - U_1 + L' + dL'),$$

and we therefore get by subtraction

$$dQ' = A(dU + dL'),$$

or, because  $dL' = p' dv$ ,

$$dQ' = A(dU + p' dv), \quad . \quad . \quad . \quad . \quad . \quad (52a)$$

or

$$dQ' = A[dF(p, v) + p' dv]. \quad . \quad . \quad . \quad . \quad (52b)$$

Now in the last two equations we have already given the fundamental formulas for the non-reversible operation.

The law of heat supply is determined as soon as the course of both pressure curves is given, and conversely one of the pressure curves can be determined when the law of the heat supply and the other pressure curve are given. Generally the question is to determine the total quantity of heat  $Q'$  necessary for a finite change; it is not then necessary to first determine the course of the pressure curve for equilibrium, provided we know  $p_1, v_1$ , and

$p_2, v_2$ , the pressure and volume for the condition of equilibrium at the beginning and at the end. In this case we have, as in equation (51), the heat quantity

$$Q' = A(U_2 - U_1 + \int_{v_1}^{v_2} p' dv),$$

where naturally the course of the curve of working pressure must be known.

Beside this procedure for the determination of the heat quantity  $Q'$  there is still another which was first given by Clausius,<sup>1</sup> and of which I myself have made considerable use<sup>2</sup> in handling technical problems.

If the body is brought from the state  $a_1$  to the state  $b_1$  (Fig. 16) by any reversible path  $a_1d_1b_1$  instead of by the non-reversible path  $acb$ , and if in so doing the heat  $Q_1$  is necessary and there is produced an external work  $L_1$ , represented by the area underneath the (dotted) curve  $a_1d_1b_1$ , then there subsists the equation

$$Q_1 = A(U_2 - U_1 + L_1).$$

Now if we consider a cycle composed in the first part of the non-reversible path  $acb$ , and in the second and returning part of any reversible path  $b_1d_1a_1$ , then  $Q_1$  is negative in the preceding equation, and its combination with equation (52) gives

$$Q' - Q_1 = A(L' - L_1),$$

or

$$Q' = Q_1 - A(L_1 - L'),$$

and from this formula can also be computed the quantity of heat  $Q'$  corresponding to the non-reversible part of the cycle, provided we know the work  $L'$  corresponding to this part. The difference  $L_1 - L' = L$  corresponds to the work expended with this

<sup>1</sup> Clausius, "Abhandlungen." Anwendung der mechan. Wärmetheorie auf die Dampfmaschine. See also Poggendorff's Annalen, 1856, Vol. 97.

<sup>2</sup> "Über die Wirkung des Drosselns," Civilingenieur, Vol. 21, 1875. "Calorimetrische Untersuchung der Dampfmaschinen," Civilingenieur, Vol. 27 and 28, 1881 and 1882.



For the non-reversible procedure let  $Q'$  again represent the heat imparted and  $L'$  the external work. .

But we can also pass from  $a_1$  to  $b_1$  in a reversible manner along the very same curves.

First conceive the body to be brought from  $a_1$  to  $a$  (Fig. 17a) under constant volume  $v_1$ , then in a reversible manner along the path  $acb$  to  $b$ , and, finally, under the constant volume  $v_2$  belonging to  $b$ , brought to the state  $b_1$ ; the three pieces of curve appear transformed in Fig. 17b, each point being computed for the magnitudes  $P=\phi(p, v)$  and  $S=f(p, v)$ , which are laid off as abscissa and ordinate respectively. Now, according to the proposition developed above, the quantity of heat  $Q_1$  to be withdrawn along the path  $a_1a$  is represented in units of work by the area  $P_1'aa_1P_1$  (Fig. 17b). The areas  $P_1'abP_2'$  and  $P_2'bb_1P_2$  likewise give, in units of work, the quantities  $Q_2$  and  $Q_3$  (imparted) during the paths  $acb$  and  $bb_1$ .

The whole hatched area (Fig. 17b) therefore represents the value

$$\frac{Q_2 + Q_3 - Q_1}{A},$$

but a part of the area is positive and the other part is negative; the planimetric determination of the area gives at once the difference, and consequently the value of the preceding expression.

Returning to the starting-point of the discussion, and assuming that the body passes along the non-reversible path from  $a_1$  to  $b_1$ , it can then be brought back to the initial condition along the reversible path  $b_1bcaa_1$ .

During the forward motion the quantity of heat  $Q'$  is supplied, and during the return motion the quantity of heat  $Q_2 + Q_3 - Q_1$  is withdrawn; but as the same quantity of work  $L'$  was produced during the forward motion as was expended during the return motion we have, as in equation (54),  $\Sigma(L)=0$ , and we therefore get

$$\Sigma(Q)=0,$$

or

$$Q' - (Q_2 + Q_3 - Q_1) = 0,$$

that is,

$$\frac{Q'}{A} = \frac{Q_2 + Q_3 - Q_1}{A}, \quad . . . . . (55)$$

hence the hatched area in Fig. 17*b* represents (in units of work) the quantity of heat  $Q'$  consumed during this non-reversible change from  $a_1$  to  $b_1$ .

Returning to the initial condition by any reversible path  $b_1d_1a_1$  (Fig. 17*a*), the transformation  $b_1d_1a_1$  (Fig. 17*b*) encloses an area  $P_1a_1b_1P_2$ , which represents (in units of work) the quantity of heat withdrawn during this return. If we suppose this area (taken as negative) to be combined with the hatched portion there will remain the area enclosed by the curved quadrilateral  $a_1b_1ba$ , which represents, therefore, the heat generated during this non-reversible cycle; but as the amount of this area corresponds to the area  $a_1b_1ba$  of Fig. 17*a*, representing the work expended, then from this also follows the proposition of Clausius which was discussed when equation (54) was established.

## § 17. HEAT WEIGHT OR ENTROPY IN NON-REVERSIBLE OPERATIONS.

For the non-reversible operation (Fig. 16, p. 75) equation (52) gives the elementary quantity of heat to be supplied:

$$dQ' = A(dU + p' dv),$$

where  $U = F(p, v)$  belongs to the point  $c_1$  of the corresponding equilibrium-pressure curve. On the other hand, if the transition of the body takes place along the equilibrium-pressure curve  $a_1c_1b_1$ , that is, in reversible fashion, then at the point  $c_1$  there will be needed the quantity of heat  $dQ$  for the expansion  $dv$ , according to the formula

$$dQ = A(dU + p dv).$$

If we subtract these equations from each other there results

$$dQ' = dQ - A(p - p')dv,$$

and if we divide both sides of this expression by  $AS$ , where  $S = f(p, v)$  corresponding to the point  $c_1$  of the equilibrium-pressure curve, we get

$$\frac{dQ'}{AS} = \frac{dQ}{AS} - \frac{(p-p')dv}{S} \dots \dots \dots (56)$$

The first term of the right member is always a complete differential whose integral is designated by  $\phi(p, v)$ , and called the heat weight. But since the course of the two curves  $acb$  and  $a_1c_1b_1$  and also the work of the equilibrium-pressure curve are to be regarded as given, then the second term of the right member of the preceding equation is also integrable.

If we designate the latter integral for the passage from  $a_1$  to  $b_1$  by  $N$ , that is, if we put

$$N = \int \frac{(p-p')dv}{S}, \dots \dots \dots (57)$$

there follows

$$\int \frac{dQ'}{AS} = \int \frac{dQ}{AS} - N,$$

or, using the designation on page 44,

$$\int \frac{dQ'}{AS} = P_2 - P_1 - N.$$

Now if we lead the body back to the initial condition along any path  $b_1d_1a_1$  (Fig. 16), we have  $P_2 = P_1$ , and therefore

$$\int \frac{dQ'}{AS} = 0; \dots \dots \dots (58)$$

consequently there follows for the non-reversible cycle:

$$\int \frac{dQ'}{AS} = -N, \dots \dots \dots (59)$$

in whatever manner the return motion may take place, because it is always reversible with com-



pression. On the other hand, equation (58) is valid for a cycle in which all parts are reversible.

These latter propositions are likewise due to Clausius, only here a different path was pursued in the development, which, at the same time, through equation (57), brought out for  $N$  a particular and clear meaning, at least for the non-reversible operations.

During the preceding investigations only the simplest and most obvious case was treated for the non-reversible operation and for the non-reversible cycle, but the propositions thus established also furnish the basis for future investigations of other non-reversible operations as they occur in the discussion of heat engines.

The occurrences in a reversible cycle, and particularly in the Carnot cycle, were compared on page 55 with the slow and uniform lifting and lowering of a body under the action of gravity. The place of the body's weight  $G$  was taken by the heat weight or entropy

$$P = \int \frac{dQ}{AS},$$

and the place of the heights  $H_1$  and  $H_2$  of Fig. 10, page 55, was taken by  $S_1$  and  $S_2$ .

The analogy can now be easily transferred to the non-reversible operation. If at the upper level  $H_1$  the weight  $G$  is slowly slid along into position this corresponds to a supply of the work  $W_1 = GH_1$ . If the weight does not sink uniformly but in an accelerated fashion to the lower level  $H_2$ , then the work there to be drawn away is  $W_2 = G(H_2 + x)$ , where  $x$  is the velocity head corresponding to the velocity attained at the lower level  $H_2$ , and  $Gx$  is the kinetic energy existing there. The produced work  $L$  amounts to  $L = W_1 - W_2$ , and from the expressions given for  $W_1$  and  $W_2$  there follows

$$\frac{W_1}{H_1} - \frac{W_2}{H_2} = -\frac{Gx}{H_2},$$

or, using  $W_1 = GH_1$ ,

$$\frac{W_2}{H_2} = \frac{W_1}{H_1} \left( 1 + \frac{x}{H_2} \right),$$

When the sinking takes place slowly and uniformly we have  $x=0$ ; we have then the reversible operation as in the Carnot cycle. (See equation IVa, page 55.)

In the non-reversible operation  $x>0$ ; therefore, according to the preceding formula, the heat weight or the entropy at the lower level is greater than at the upper level, and becomes a maximum for  $x=H_1-H_2$  and consequently for  $W_2=W_1$  and  $L=0$ ; the case corresponds to the free falling of a weight, to the direct passing of heat from a body of higher to one of lower temperature, to heat conduction, and  $Q_2=Q_1$ , if we express the quantity of work  $W_2$  and  $W_1$  in units of heat.

Since a weight tends toward the lower level we can also say, according to the preceding, "entropy tends toward a maximum"; then, because this analogy, here developed for a particular case, can easily be extended to any cycle, we arrive at the proposition enunciated by Clausius for heat—"The entropy of the world tends toward a maximum," a proposition which, to be sure, seems very trivial, but, according to our analogy, can be compared with the statement that all the water existing on the earth tends toward the level of the sea. In the one case as in the other the proposition thus generally stated possesses no special value as a basis for future investigation.

For the reversible cycle our analogy is complete in every respect; for the non-reversible operation, on the other hand, as Helm<sup>1</sup> properly emphasizes, it is only true when we regard the kinetic energy at the lower level as lost, but that is always the case in hydraulic motors.<sup>2</sup>

<sup>1</sup> G. Helm, "Die Energetik," Leipsic, 1898, p. 259.

<sup>2</sup> The comparison of the cycle events in thermodynamics with a raising and lowering of weight was made in the earlier (1866) edition of the present book. Later Mach, at least for reversible operations, went more fully into the question (in a short note as early as 1871 and fully in 1892, Wiener-Sitzungsberichte, p. 1589.—"Die Principien der Wärmelehre," Leipsic, 1896).

## CONCLUSION.

Let us once more briefly return to the general consideration of the reversible cycle on page 47. There we can conceive the closed curve between the two limiting adiabatics  $P_1$  and  $P_2$  (Fig. 7b) to be traversed by an infinite number of adiabatics lying close together; each elementary strip corresponds to an elementary Carnot cycle like the one represented for finite changes in Fig. 8, p. 52. But considering one such strip we have for every passage from one adiabatic to the next the constant magnitude

$$dP = \frac{dQ}{AS},$$

and from this follows, when we measure the quantities of heat  $dQ$  in units of work, and designate them by  $dW$ , so that  $dW = 1/A \, dQ$ ,

$$dW = S \cdot dP. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

If at the upper limit  $S = S_1$ , and at the lower  $S = S_2$ , then the quantity of heat or work or energy supplied at the upper limit is  $dW_1 = S_1 dP$ , and the amount withdrawn at the lower limit is  $dW_2 = S_2 \cdot dP$ ; also the work produced by traversing the cycle is

$$dL = (S_1 - S_2) dP. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

In the heat cycle  $dP$  is the heat weight, or entropy, and  $S$  a function of temperature having the property  $S_1 > S_2$  when the temperature  $t_1 > t_2$ . In our repeatedly discussed analogy,  $dP$  is the weight of the body and  $H$  the height of the plane above a given datum plane; in both cases  $dW$  is the disposable energy at the level  $S$ .

But the two formulas  $(\alpha)$  and  $(\beta)$  have a more general significance than appears from the foregoing. Thus for some time past attention has been called to the fact that when the electrical current moves in a conductor the term  $dL$  in equation  $(\beta)$  represents the work necessary to overcome the resistance in the conductor (which work is converted into heat), but, on the other hand, that this differential of  $L$  represents the work of an electromotor when

$dP$  means the quantity of electricity or strength of the current (in amperes), and  $S_1 - S_2$  the difference of potential or electromotive force (in volts); the quantity  $S$  represents nothing but the potential function, and  $dW$  its corresponding (electrical) energy, and it is these simple formulas which we employ in electrical engineering for the computation of great electrical plants and power transmissions and utilize in the most extended fashion in judging heat engines, particularly steam engines—and this occurs although the electrical and mechanical engineer, as well as the physicist, has no real conception of the nature of electricity or of heat; it completely suffices to assume that in both cases we are dealing with certain forms of energy.

If in equation ( $\alpha$ ) we consider the magnitude  $S$  as a height and  $dP$  as a weight, and if we multiply the force by the specific weight  $\gamma$ , then  $S$  appears as a pressure upon the unit of area, which may be designated by  $p$ ; on the other hand  $dP$  divided by  $\gamma$  represents the volume which may be designated by  $dv$ .

Equation ( $\alpha$ ) then takes the form

$$dW = p \, dv, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha')$$

a relation which has already been considered by others from this same point of view, and in so doing  $W$  has been designated as volume-energy.

If at the upper limit  $p=p_1$ , and at the lower limit  $p=p_2$ , then the supplied energy is  $dW_1=p_1dv$ , the drawn-away energy  $dW_2=p_2dv$ , and the corresponding work produced during the change

$$dL = (p_1 - p_2)dv, \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta')$$

which is entirely in accordance with formulas ( $\alpha$ ) and ( $\beta$ ). The question here indicated was first treated by HELM in the most general manner for the different forms of energy.<sup>1</sup> The magnitude  $S$  of the above equation ( $\alpha$ ) he designates by  $J$  and calls it intensity, and the magnitude  $P$ , which he designates by  $M$ , he

<sup>1</sup> George Helm, "Die Lehre von der Energie," Leipsic, 1887, as well as in the already mentioned treatise "Energetik." With respect to the propositions emphasized in the text see reference to the comparisons instituted in the former book, p. 62, and in the latter book, p. 291.

calls the quantity function and later on "Extensity" ("Energetik," p. 266), and then enunciates the proposition "That every form of energy has a tendency to pass from the position in which it exists at the higher intensity to a position of lower intensity. It is said to be released when it can obey this tendency."

SECOND SECTION.

**Theory of Gases.**



## § 18. PRELIMINARY REMARKS.

During a comparatively recent period those kinds of air which were only known to exist in the air-like condition were discussed as "gases," or also as "permanent gases." This was the case whenever they could not be brought into the liquid condition by any means, say by great compression and simultaneous cooling; it was then naturally assumed that they were not originally produced by "evaporation" from liquid and solid bodies. But long ago and repeatedly the thought was expressed that it was highly probable that the so-called permanent gases did not exist, and it was simply the insufficiency of the means for producing unusually great reductions of temperature which rendered it apparently impossible to bring back such gases to the liquid condition. This view has quite recently received full confirmation by the experiments of Raoul Pictet, Cailletet, von Wroblewski, and Olszewski, who succeeded in liquefying even those gases which up to that time had usually been regarded as the principal representatives of the "permanent gases."

Finally, great and wide-spread interest was created by the brilliant results of the experiments of Linde and Dewar, particularly by those of Linde, on account of the cleverly conceived and constructed machine for liquefying atmospheric air on a large scale in a purely mechanical way.

In doing this the first step was taken to utilize laboratory experiments in a large way for industrial purposes. Later in this book Linde's procedure will be fully explained.

Under these circumstances it now seems to be time to designate and treat all kinds of gases without exception as "vapors";



if in the whole arrangement of this treatise, however, we still maintain the difference between gases and vapors, we must justify this procedure in what follows. At present the remark may suffice that we conceive gases to be only a special condition of vapors and regard the adjective "permanent" as inadmissible.

If we supply heat under invariable pressure to a solid body, say to a piece of ice, then at a particular temperature this ice will gradually pass into the liquid condition (will melt), till it has all become water; with a further supply of heat, always under the same pressure and therefore accompanied by a corresponding change of volume, evaporation will begin, until finally the water has evaporated into steam, into the gaseous condition. If, while maintaining the aforesaid condition, the heat supply is still continued, then this steam (which we will designate as "superheated steam") will show properties very much like those which have hitherto been regarded as peculiar to the permanent gases.

The conclusion seems obvious that gases are nothing but "highly superheated vapors," and that we may here conceive of a certain limiting condition in which complete agreement is realized and the well-known law of *M a r i o t t e* and *G a y - L u s s a c* is followed, which law, moreover, will be discussed later.

This limiting condition is designated as the one in which the ideally perfect gas exists, and is distinguished from that other limiting condition in which the steam is still in contact with the liquid (in this case the water) out of which it is formed. In this latter condition, the so-called "state of saturation," the steam exhibits the peculiar property of the temperature remaining constant so long as the pressure is constant. In spite of the heat supply and the corresponding expansion of the total mass this behavior continues as long as any liquid is on hand; not until the last element of the liquid has been evaporated will the further increase of temperature begin, and this will continue until the ideal gaseous condition is reached.

A similar behavior also accompanies the passage from the solid to the liquid condition; now returning to the illustration assumed above, as long as ice is present with the water during the

melting period the temperature will remain constant while the pressure remains constant, provided the corresponding change of volume is possible. Not until the last element of ice has been converted into water will the continued supply of heat raise the temperature and raise it to that point at which evaporation begins; and from this time on the circumstances shape themselves in the manner first described.

The definition of a gas as highly superheated vapor, or as vapor which is far removed from its point of condensation, is by no means as definite as it seems at the first moment.

If a vapor shut off from its liquid, and in the condition we call superheated, receives still more heat, then there occurs, at a particular temperature, a new and significant change called "dissociation" which can be regarded as a chemical change of state, as decomposition, resolution, or breaking-up of the steam into its constituent parts; and these constituents can in turn be compound vapors or the elementary constituents of the decomposed vapor. Thus water-vapor decomposes into its constituents hydrogen and oxygen; the formation of the so-called "water-gas" is effected by allowing the vapor of water to pass through glowing coal; this gas is already widely used for heating purposes, and its general use for purposes of illumination is probably only a question of time.

Dissociation therefore seems to be a procedure analogous to fusion and evaporation. Return again to the example of ice and imagine it to be at  $0^{\circ}$  C.; for the sake of simplicity consider it to be at atmospheric pressure during the various parts of its changes of state while heat is supplied, then melting will occur at  $0^{\circ}$  C., and this temperature will be maintained till the fusion is completed; now the temperature will begin to rise up to  $100^{\circ}$  C., until the commencement of the evaporation. This temperature in turn is maintained constant until the last element of water is evaporated, and now will begin the further rise of temperature until the commencement of dissociation. It has not yet been decided whether or not from here on to the end of dissociation the temperature remains constant, so long as the assumed atmospheric pressure is constant; fusion and evaporation are purely physical

procedures, and dissociation is at the same time a chemical process, and therefore it is quite possible that, according to the present prevailing views, the whole course of the dissociation takes place under increasing temperatures; doubtless the law of change of the temperature will be different from what it was before the beginning of the dissociation, and different from what it is after the end of the dissociation, even though we assume equal quantities of heat to be supplied in the cases compared.

In like manner the changes of volume during, before and after dissociation are subject to laws which differ from those which obtain during, before and after either evaporation or fusion.

There is still a complete lack of suitable experiments with respect to the process of dissociation; but this much may be expected, that in general during the dissociation (other things being equal) the increase of volume under constant pressure will take place more rapidly than before the beginning of the dissociation.

What has hitherto been said for this case of water in its various states of aggregation also holds for a whole series of other bodies; but bodies do occur in which certain intermediate stages of the changes of state considered, disappear. Thus some bodies pass directly from the solid to the vapor condition without any preliminary fusion, while certain other bodies do not even possess the intermediate stages of evaporation, but experience immediate dissociation.

Concerning the temperature of dissociation, or, to speak more exactly, concerning the temperature at the beginning of dissociation, there are at present very few observations; but we may say that it seems probable that certain gases dissociate, in whole or in part, at a comparatively low temperature, say at the atmospheric temperature; in the latter case they may be considered as consisting of a mixture of gases rather than of a gas of uniform chemical constitution throughout; but there are reasons for thinking that for those vapors which we will hereafter specially treat as gases a partial dissociation does not take place during the, to be sure, narrow range of temperatures assumed.

On the basis of the foregoing remarks we will now briefly designate as *gas* a superheated steam which before the beginning of dissociation obeys the law of *Mariotte* and *Gay-Lussac*, which law will be more fully discussed later on. At the same time the last modifying clause indicates that there may be vapors which at no point of their changes of state can be treated as gases, in the sense defined, unless it is after completing the dissociation, in which case vapor of the original chemical combination will not be before us.

The proof that gases do exist which satisfy the given definition is of the highest importance for thermodynamics; only under the assumption of the existence of such gases can we deduce the form and meaning of that temperature function which was designated above in § 12, p. 61, as the *Carnot* function. It was proved that this function was numerically the same for all bodies without any exception whatever. Nevertheless, no one has yet succeeded in deriving the form of this function from the physical behavior of solids, liquids, or vapors in general.

Now in fact we do know some gases and mixtures of gases, to which latter atmospheric air belongs, which correspond to the given definition, and therefore it is justifiable in Thermodynamics to distinguish between gases and vapors, all the more as the equations of the mechanical theory of heat applied to gases have simpler and clearer forms than with vapors.

## § 19. EQUATION OF CONDITION FOR GASES.

The equation of condition for a gas (§ 12, p. 62) expresses the relation between the specific volume, the pressure  $p$ , and the temperature  $t$ , and is given in Physics as the mathematical expression of the combined laws of *Mariotte* and *Gay-Lussac*.

According to *Mariotte* or *Boyle* the pressure of a gas is inversely proportional to the volume when the gas expands or contracts under constant temperature, the product  $pv$  remaining constant under these conditions.

But if the initial condition is given by  $p_1$  and  $v_1$ , then, according to *Mariotte*, we get the relation

$$pv = p_1v_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which represents an equilateral hyperbola when  $v$  is laid off as abscissa and  $p$  as ordinate; and as the temperature is here assumed to be constant, the foregoing expression at the same time represents the "isothermal curve" for gases (§ 6, p. 39) passing through the point  $(p_1, v_1)$ .

The other law, that of *Gay-Lussac*, says that the increment of volume of a gas is proportional to the increment of temperature when the expansion of a gas takes place under constant pressure while the gas is being heated.

Let  $\alpha$  represent the expansion of a unit of volume of a gas when it is heated  $1^\circ \text{C.}$  [ $1^\circ \text{F.}$ ] under the assumption made, then  $\alpha t$  [ $\alpha(t - 32^\circ)$ ] is the increment of volume for heating from  $0^\circ \text{C.}$  [ $32^\circ \text{F.}$ ] to  $t^\circ$ ; let us designate by  $v_0$  the volume of the gas at  $0^\circ \text{C.}$  [ $32^\circ \text{F.}$ ] and its volume at  $t^\circ$  by  $v$ , thus getting

$$v = v_0(1 + \alpha t) \\ [v = v_0[1 + \alpha(t - 32^\circ)]],$$

and likewise for the volume  $v_1$  at temperature  $t_1$

$$v_1 = v_0(1 + \alpha t_1) \\ [v_1 = v_0(1 + \alpha(t_1 - 32^\circ))].$$

Dividing one of these by the other we get the expression for *Gay-Lussac's Law*:

$$\frac{v}{v_1} = \frac{1 + \alpha t}{1 + \alpha t_1} \\ \left[ \frac{v}{v_1} = \frac{1 + \alpha(t - 32^\circ)}{1 + \alpha(t_1 - 32^\circ)} \right],$$

and this will be true for any pressure whatever provided it is constant.

The value  $\alpha$  is called the coefficient of expansion of the gas; if we divide the numerator and the denominator of the right-hand member by  $\alpha$  and call  $a$  the reciprocal of  $\alpha$ , then we get

$$\frac{v}{v_1} = \frac{a+t}{a+t_1} \dots \dots \dots (2)$$

$$\left[ \frac{v}{v_1} = \frac{a+(t-32^\circ)}{a+(t_1-32^\circ)} \right]$$

If the initial condition of the unit of weight of a gas is given by the magnitudes  $v_1 p_1 t_1$  (Fig. 18), and if the gas expands under constant pressure  $p_1$  and heat supply from  $v_1$  to  $v_m$ , then we have, according to equation (2), the relation

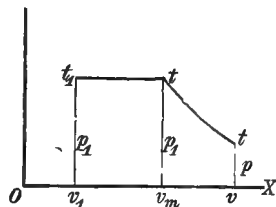


FIG. 18.

$$\frac{v_m}{v_1} = \frac{a+t}{a+t_1}$$

$$\left[ \frac{v_m}{v_1} = \frac{a + (t - 32^\circ)}{a + (t_1 - 32^\circ)} \right]$$

Now if we allow the gas to continue its expansion under constant temperature  $t$  from  $v_m$  to  $v$  (which likewise requires suitable heat supply), then the pressure will fall from  $p_1$  to  $p$ , and according to equation (1) we have the relation

$$pv = p_1 v_m.$$

If we eliminate from the last two expressions the intermediate volume  $v_m$ , we get

$$\frac{pv}{a+t} = \frac{p_1 v_1}{a+t_1} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (3)$$

$$\left[ \frac{pv}{a + (t - 32^\circ)} = \frac{p_1 v_1}{a + (t_1 - 32^\circ)} \right].$$

If  $a$  were experimentally determined and if for a particular gas the necessary temperature  $t_1$ , the pressure  $p_1$ , and the

volume  $v_1$  had been observed, we could compute the right member of the foregoing equation; if we designate the value of this member by  $B$ , then the equation can be written as follows:

$$pv = B(a+t) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

$$[pv = B[a + (t - 32^\circ)]] ,$$

and this is the equation of condition for gases, which at the same time expresses in the simplest form the laws of Mariotte and Gay-Lussac. This form of the equation of condition was used by Clapeyron.

Now as regards the constants  $a$  and  $B$  of the equation of condition for gases we will first discuss the constant  $a$ .

If we compute  $a$  from equation (3), we get

$$a = \frac{p_1 v_1 t - p v t_1}{p v - p_1 v_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\left[ a = \frac{p_1 v_1 t - p v t_1}{p v - p_1 v_1} + 32 \right] .$$

The experiments on this point have been conducted in two-fold fashion; either the pressure  $p$  was maintained constant and the volume observed at the temperatures  $t$  and  $t_1$ , or the volume was kept constant and the pressures  $p$  and  $p_1$  were determined for the corresponding temperatures.

If we designate by  $a_p$  the value of  $a$  derived from the experiments under constant pressure, and by  $a_v$  the value of  $a$  for constant volume (the subscript  $p$  or  $v$  indicating that in the experiments in question the designated magnitude is kept constant), then there follows from equation (4), respectively for  $p = p_1$  and  $v = v_1$ ,

$$a_p = \frac{v_1 t - v t_1}{v - v_1} \quad \text{and} \quad a_v = \frac{p_1 t - p t_1}{p - p_1} \quad . \quad . \quad . \quad . \quad (5)$$

$$\left[ a_p = \frac{v_1 t - v t_1}{v - v_1} + 32 \quad \text{and} \quad a_v = \frac{p_1 t - p t_1}{p - p_1} + 32 \right] .$$

If in both cases we imagine an infinitesimal change of temperature  $dt$  as occurring, then we get, as may easily be seen,

$$a_p = v \frac{\partial t}{\partial v} - t \quad \text{and} \quad a_v = p \frac{\partial t}{\partial p} - t \quad . \quad . \quad . \quad (6)$$

$$\left[ a_p = v \frac{\partial t}{\partial v} - (t - 32^\circ) \quad \text{and} \quad a_v = p \frac{\partial t}{\partial p} - (t - 32^\circ) \right].$$

Under the supposition that the equation of condition is exactly correct both experimental methods should lead to one and the same value  $a$  for  $a_p$  and  $a_v$ , which is not the case; we must therefore conclude that the above equation of condition can only be regarded as an approximate form. Now there are, to be sure, gases in which the deviations are so slight that, without any hesitation whatever, one can regard equation (3) as rigidly exact; and it is just these gases which we will hereafter especially designate as gases, in accordance with the remarks already made in § 18, p. 93. To these gases belong atmospheric air, which we will always put first on account of its great technical importance, although it is no simple gas but a mixture of two gases, Oxygen and Nitrogen. The mechanical mixture of such simple gases as Hydrogen, Oxygen, and Nitrogen, and also the chemically compound gases, nitric oxide and carbonic oxide, will be regarded as obeying the law on account of their insignificant deviations from it.

According to the experiments of *Regnault*,<sup>1</sup> for pressures deviating but little from atmospheric pressure and with temperature limits 0 to 100° C. there were obtained, after a corre-

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<sup>1</sup> *V. Regnault*, "Relation des expériences pour déterminer les principales lois et les données numériques qui entrent dans le calcul des machines à vapeur." Paris.

This classic work in three volumes, of which the first volume appeared in 1847, the second in 1862, and the third in 1870, contains the results of the numberless wonderful experiments of *Regnault*. For the development of thermodynamics, and particularly in its technical direction, the work of *Regnault* is of inestimable value—*Henry Victor Regnault*, born July 21, 1810, in Aix-la-Chapelle, died January 19, 1878, in Auteuil.

This work of *Regnault* will, in the further course of this book, be so often referred to that we will designate it simply by *Rel.*, the volume by Roman numerals, and the page by Arabic numerals.



sponding recomputation of *Regnault's*<sup>1</sup> data, for the magnitudes  $a_p$  and  $a_v$  the following values:

	French Units.		English Units.	
	$a_p$	$a_v$	$a_p$	$a_v$
Atmospheric Air.....	272.48	272.85	490.46	491.13
Hydrogen.....	273.15	272.70	491.67	490.86
Nitrogen.....	.....	272.63	.....	490.73
Carbonic Oxide.....	272.52	272.70	490.54	490.86
Carbonic Acid.....	269.54	271.15	485.17	488.07
Nitrous Oxide.....	268.89	272.03	484.00	489.65

(For Oxygen we would have to assume  $a_v = 272.18$  according to *Jolly's* data.)  
[ $a_v = 489.92$ .]

The numerical values show that with the exception of hydrogen the values of  $a_v$  are greater than the values of  $a_p$  for all gases, but that for the earlier tabulated gases the difference is insignificant. Only for carbonic acid and nitrous oxide are the differences considerable; but these are gases which are far nearer to their points of condensation, and can therefore not be designated as gases. In another experimental series *Regnault*<sup>2</sup> observed the diminution of volume for the following gases at different but constant pressures; the pressures measured in millimeters of mercury gave the following values for  $a_p$ :

	Pressure.	Value of $a_p$ .	[Value of $a_p$ .]
Atmospheric Air.....	760	272.43	490.37
	2525	270.68	487.22
	2620	270.53	486.95
Hydrogen.....	760	273.13	491.63
	2545	273.10	491.58
Carbonic Acid.....	760	269.55	485.19
	2520	260.04	468.07

Here we again see the anomalous behavior of carbonic acid, and also see that the value of  $a_p$  seems to be smaller at the higher pressures.

Other investigations of *Regnault* related to atmospheric air and carbonic acid; the volume was kept constant

<sup>1</sup> Rel. I, 91.

<sup>2</sup> Rel. I, 115, 116, 117.

and different initial pressures at 0° C. were employed, and then a corresponding final pressure was observed at 100° C. From the second of the equations (5) and from R e g n a u l t ' s data the values of  $a_v$  in the following tabulations have been derived:

ATMOSPHERIC AIR.<sup>1</sup>

Pressure.		French Value of $a_v$	English Value of $a_v$
At 0° C. [At 32° F.] mm.	At 100° C. [At 212° F.] mm.		
109.72	149.31	274.11	493.40
174.36	237.17	273.87	492.97
266.06	395.07	273.65	492.57
374.67	510.35	273.32	491.98
375.23	510.97	273.43	492.17
760.00	—	272.85	491.13
1678.40	2286.09	272.03	489.65
1692.53	2306.23	271.96	489.53
2144.18	2924.04	271.05	487.89
3655.56	4992.09	269.61	485.30

CARBONIC ACID.<sup>2</sup>

Pressure		French Value of $a_v$	English Value of $a_v$
At 0° C. [At 32° F.]	At 100° C. [At 212° F.]		
785.47	1034.54	271.33	488.39
901.09	1230.37	270.68	487.20
1742.73	2387.72	266.50	479.70
3589.07	4759.03	259.08	466.34

We see from this experimental series that with the same limiting temperatures the value  $a_v$  diminishes as the initial pressure increases, and a similar result was evident in the foregoing tabulation of the values  $a_p$ . The greater the pressure for the same temperature, the denser is the gas and the closer to one another will be the gas molecules. Now as the molecules act upon each other with certain forces, which doubtless grow very rapidly with diminishing distances, the thought lies nigh to ascribe to this circumstance the deviations exhibited by the gases from the behavior assumed when establishing the above equation of condition (3a). We further conclude that these deviations become the smaller the more rarefied the gas, and that the condition is finally attained in which the molecules have passed beyond the mutual

<sup>1</sup> Rel. I, 110.<sup>2</sup> Rel. I, 112.

attraction of their spheres of action, or, to speak more exactly, in which these forces may be regarded as infinitesimal during the future changes of state of the gas; in this sense we speak of an ideal gas, and for such a gas the differences, shown by experiments for the magnitudes  $a_p$  and  $a_v$ , disappear, and both values should approach for all gases that particular determinate value of  $a$  which has been introduced into the equation of condition.

Disregarding for the present the values given for carbonic acid and nitrous oxide, and now directing our attention to the first two of the above given four tabulations of *Regnault's* experimental results, we see that for atmospheric air, hydrogen, and carbonic oxide the differences between  $a_p$  and  $a_v$  are very small; if furthermore we consider that hydrogen has, other things being equal, the slightest density among all the gases, and that for it the two values  $a_p$  and  $a_v$  differ least from one another and approximately show the value 273, then it seems thoroughly justifiable that we should assume this value, generally, as the limiting value. The third of the above tabulations shows that *Regnault* found for atmospheric air, under the least pressure occurring in his experiments, that the value of  $a_v$  turned out to be somewhat greater than 274, which has caused some authors to assume this value as the limiting value. But the circumstance that the first limiting value is generally accepted, and furthermore that the assumption of the one or the other limiting value causes only an insignificant difference in the computations (such slight differences can always be neglected in technical investigations, and can be disregarded in most cases in the more refined physical discussions), is the reason why, in all future investigations, the limiting value

$$a = 273$$

$$[a = 491.4]$$

will be retained; this was done by *Clausius* in all his papers.

If we substitute this limiting value in the equation of condition (3a), we get

$$pv = B(273 + t)$$

$$[pv = B(459.4 + t)],$$

and from this it is evident that a new zero-point of the thermometric scale has been obtained which in a certain sense is prescribed by nature herself. As the freezing-point of water at atmospheric pressure serves as a starting-point for measuring the temperature  $t$ , according to Celsius, so that point of the thermometric scale lying  $273^{\circ}\text{C}$ . [ $491.4^{\circ}\text{F}$ .] under the freezing-point, can in like manner serve as the starting-point for the measurement of temperature; we call this point the absolute zero, and the corresponding temperature  $a+t=273+t$  [ $a+t=459.4+t$ ], the absolute temperature of the body in question.

The equation of condition (3a) assumes that the volume  $v$  refers to the unit of weight of the gas in question; but if in the space  $V$ ,  $G$  kilograms ( $G$  pounds) are enclosed, then

$$V=Gv,$$

and therefore if both members of equation (3a) are multiplied by  $G$  we get

$$Vp=GB(a+t). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation is the handiest one for computing the weight of a gas enclosed in a given space of  $V$  cbm. ( $V$  cu. ft.) at pressure  $p$  and temperature  $t$ , provided we know the constant  $B$  for the gas in question.

If the capacity of the space  $V$  is just one cbm. (one cu. ft.), then  $G$  is the weight of a cubic unit of gas at the existing pressure  $p$  and its corresponding temperature  $t$ , and this weight we will, in what follows, always designate by  $\gamma$ , and call it the specific weight of a gas. Equation (7) gives, therefore,

$$\frac{p}{\gamma}=B(a+t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and from this follows, by combination with (3a), the following relation between the specific volume  $v$  and the specific weight  $\gamma$ ,

$$v\gamma=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It deserves to be emphasized that a special meaning can be said to underlie the two forms of the equations of condition (3a) and (8). The product  $pv$  represents the equation of work which is necessary to fill or empty the space  $v$ ; this work is accordingly proportional to the absolute temperature  $a+t$ .

On the other hand, in equation (8)  $p : \gamma$  represents the height of a column of gas whose specific weight is everywhere  $\gamma$  and which by means of its weight exerts upon every unit of area of its base the pressure  $p$ .

If we assume that equation (8) holds good for a particular gas, then for another gas, of a similar pressure  $p$  and the same temperature  $t$ , the specific weight  $\gamma$  and the constant  $B$  will assume another value; if we designate these values respectively by  $\gamma_0$  and  $B_0$ , then we also have

$$\frac{p}{\gamma_0} = B_0(a+t),$$

and if we divide this equation by equation (8) there follows

$$\frac{\gamma}{\gamma_0} = \frac{B_0}{B}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This ratio, which in the future we will designate by  $\epsilon$ , is the weight of one gas relatively to the other.

Hereafter the relative weight of gases will always be referred to hydrogen. It follows, therefore, from equation (10) that

$$B_0 = B\epsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

from which it seems that the value  $B\epsilon$  is the same for all gases and that the equation of condition for gases, equation (3a), can also be written in the form

$$pv\epsilon = B_0(a+t). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3c)$$

For dry atmospheric air Regnault<sup>1</sup> found the specific weight  $\gamma$ , i.e., the weight of a cubic meter (cu. ft.) of air

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<sup>1</sup> Rel. I, 157.

measured in kilograms (pounds) at the temperature of  $0^{\circ}\text{C.}$ , and at the average barometric pressure of 760 mm. of mercury, to be

$$\begin{aligned}\gamma &= 1.293187 \text{ kg.} \\ [\gamma &= 0.0807288 \text{ lb.}]\end{aligned}$$

in the latitude of Paris. Since, according to Regnault,<sup>1</sup> the weight of 1 cbm. of mercury amounts to 13596 kg. [1 cu. ft. weighs 848.747 lb.], then the barometric pressure of 760 mm. corresponds to a specific pressure of  $p = 0.760 \times 13596 = 10332.96$  kg. [2116.31 lb. per sq. ft.], or, accurately enough,  $p = 10333$  kg. to the square meter, which value will be hereafter designated as the "mean atmospheric pressure." Therefore with air

$$\begin{aligned}\frac{p}{r} &= 7990.34 \\ \left[ \frac{p}{r} &= 26215.03 \right],\end{aligned}$$

and from equation (8), for  $t = 0$  [ $32^{\circ}$ ] and  $a = 273$  [491.4],

$$\begin{aligned}\text{we get} \quad B &= 29.269 \\ [B &= 53.349].\end{aligned}$$

On the basis of other experiments by Regnault<sup>1</sup> the table on page 104 has been computed for those gases which more completely obey the given equation of condition.

This table gives rise to some remarks. The product  $B\epsilon$ , therefore, of the values occurring in the last two columns, is the same for all the gases enumerated, and is 422.595 [770.259]; and moreover for the same pressure and volume the product  $B\gamma$  is also the same for all gases and amounts to  $B\gamma = 37.850$  [ $B\gamma = 4.3067$ ], which value results directly from equation (8) for  $p = 10333$  [ $p = 2116.31$ ] and  $t = 0$  [ $t = 32^{\circ}$ ].

It is remarkable that the value of the first-mentioned product is almost equal to that of the mechanical equivalent of heat (424) [772.83]. That these two values are perfectly equal cannot be proved with our present knowledge of the internal constitution of

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<sup>1</sup> Rel. I, 142, 144, 145.

	Specific Weight. $\gamma$	Weight relatively to Hydrogen. $\epsilon$	Value of $B$ .
	kg.		
Atmospheric Air. ....	1.293187	14.4384	29.269
Hydrogen. ....	0.089566 = ( $\gamma_0$ )	1	422.591 = ( $B_0$ )
Oxygen. ....	1.429786	15.9635	26.472
Nitrogen. ....	1.256163	14.0250	30.131
Nitric Oxide. ....	1.34284	14.9928	28.186
Carbonic Oxide. ....	1.25090	13.9662	30.258

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	Specific Weight. $\gamma$	Weight relatively to Hydrogen. $\epsilon$	Value of $B$ .
	lb.		
Atmospheric Air. ....	0.0807288	14.4384	53.349
Hydrogen. ....	0.0055913 = ( $\gamma_0$ )	1	770.259 = ( $B_0$ )
Oxygen. ....	0.0892562	15.9635	48.251
Nitrogen. ....	0.0784175	14.0250	54.920
Nitric Oxide. ....	0.083828	14.9928	51.375
Carbonic Oxide. ....	0.078089	13.9662	55.151

bodies; nevertheless we can make use of this accidental coincidence, if we may so describe it, in certain approximate computations. As the thermal equivalent of the unit of work ( $A$ ) is reciprocal of the value 424 [772.83], we would have for hydrogen  $AB_0=1$ , and according to equation (11) for every other gas

$$AB\epsilon=1;$$

an equation of condition for gases could then be written, following equation (3a), p. 96, in the form

$$Apv\epsilon=a+t, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

so that for all gases taken at the same temperature and at the same pressure the product  $v\epsilon$  would be the same, a result moreover which follows from the combination of equations (10) and (11); the product corresponds to specific volume of hydrogen, which becomes for atmospheric pressure  $0^\circ$  [ $32^\circ$ ] temperature

$$v_0 = \frac{1}{\gamma_0} = 11.1649 \text{ cbm.}$$

$$\left[ v_0 = \frac{1}{\gamma_0} = 178.85 \right].$$

Of special importance, however, is the following remark. If we consider the numerical values of the second column in the

preceding table, leaving out atmospheric air, which is a mixture of gases, we see that these are almost exactly equal to the half values of the so-called molecular weights of the gases in question.

If we designate for the different chemical elements  $E_1, E_2$ , etc., the corresponding atomic weights by  $e_1, e_2, e_3$ , etc., and if we assume that the molecule of any chemical combination consists of  $n_1$  atoms of the first element  $E_1$ , of  $n_2$  atoms of the second element  $E_2$ , etc., then the molecular weight of this body is

$$m = n_1 e_1 + n_2 e_2 + n_3 e_3 + \dots,$$

or simply

$$m = \Sigma(ne). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

For the elements considered in the following investigations the atomic weights are as follows:

Hydrogen (H) . . .	$e = 1$	Carbon (C) . . . . .	$e = 12$
Oxygen (O) . . . . .	16	Chlorine (Cl) . . . . .	35.5
Nitrogen (N) . . . .	14	Sulphur (S) . . . . .	32

We therefore have for

Steam ( $\text{H}_2\text{O}$ ) . . . . .	$m = 2 \times 1 + 1 \times 16 = 18$
Ammonia Vapor ( $\text{NH}_3$ ) . . . . .	$m = 1 \times 14 + 3 \times 1 = 17$
Sulphuric Acid ( $\text{SO}_2$ ) . . . . .	$m = 1 \times 32 + 2 \times 16 = 64$
Carbonic Acid ( $\text{CO}_2$ ) . . . . .	$m = 1 \times 12 + 2 \times 16 = 44$

In the last tabulation, p. 104, all the gases enumerated are diatomic; if we designate the molecular weight of hydrogen by  $m_0$  ( $m_0 = 2$ ), then the gases there designated by  $\epsilon$  appear to coincide almost exactly with the values  $m : m_0$  of the following tabulation; it was Gay-Lussac who first called attention to this coincidence. The agreement also exists with all other gases. Now if we utilize the value  $\epsilon = m : m_0$  in equation (11), the constant  $B$  of the equation of condition of a gas becomes

$$B = \frac{B_0 m_0}{m} = \frac{845.182}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\left[ B = \frac{B_0 m_0}{m} = \frac{1540.52}{m} \right],$$



provided we substitute the hydrogen values  $B_0=422.591$  [770.259] and  $m_0=2$ .

In place of the last tabulation we have therefore:

	Composi- tion.	Molecular Weight.	French Value $B = \frac{B_0 m_0}{m}$	English Value $B = \frac{B_0 m_0}{m}$
Hydrogen. . . . .	H <sub>2</sub>	2 = $m_0$	422. 591	770. 26
Oxygen. . . . .	O <sub>2</sub>	32	26. 412	48. 14
Nitrogen. . . . .	N <sub>2</sub>	28	30. 185	55. 02
Nitric Oxide. . . . .	NO	30	28. 173	51. 35
Carbonic Oxide. . . . .	CO	28	30. 185	55. 02

These values of  $B$  are in satisfactory agreement with the values given on page 104 and directly determined from experiments. The utilization of relation (14) in the equation of condition gives

$$A p m v = A B_0 m_0 (a + t), \quad . \quad . \quad . \quad . \quad . \quad (15)$$

in which  $A B_0 m_0 = 1.9933$ ; this magnitude would be 2 if we were to assume  $B_0$  as identical with 424 [772.83], as recently suggested. But at any rate the foregoing equation shows that with the same pressure and the same temperature the product  $m v$  is the same for all gases. If we replace the specific volume  $v$  by the specific weight  $\gamma$ , then from what has preceded we have for two different gases the relation

$$\frac{m_1}{\gamma_1} = \frac{m_2}{\gamma_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Now if we imagine that there exist in a space  $V$  at one time  $n_1$  molecules of a gas of the molecular weight  $m_1$ , and at another time in the same space  $n_2$  molecules of the molecular weight  $m_2$ , the ratio of the weights  $G_1$  and  $G_2$  of the two quantities of gas is

$$\frac{G_1}{G_2} = \frac{n_1 m_1}{n_2 m_2}.$$

On the other hand we also have

$$\frac{G_1}{G_2} = \frac{V \gamma_1}{V \gamma_2} = \frac{\gamma_1}{\gamma_2}.$$

The combination of the two equations gives

$$\frac{n_1 m_1}{r_1} = \frac{n_2 m_2}{r_2}, \quad *$$

and, comparing this with equation (16) we draw the conclusion that  $n_1 = n_2$  must be true. It follows, therefore, that equal volumes of different gases at the same pressure and the same temperature possess the same number of molecules.

This is Avogadro's law, which is one of the most important foundation stones of the Chemistry of to-day.

## § 20. GAS MIXTURES.

The investigations concerning the behavior of mixtures, mechanical mingling of various gases, are of importance for certain technical problems, and their closer examination is therefore justified. If in a space  $V$  there exist two gases, one weighing  $G_1$  kg. [lb.] and the other  $G_2$  kg. [lb.], and if the temperature of the two gases and that of their mixture is equal to  $t$ , and if moreover the constant  $B$  of the equation of condition is equal to  $B_1$  and to  $B_2$  of the constituent gases, and if finally the pressure of the one gas is  $p_1$  and of the other  $p_2$ , then we have, according to equation (7), the two relations

$$Vp_1 = G_1 B_1 (a + t) \quad \text{and} \quad Vp_2 = G_2 B_2 (a + t), \quad . \quad . \quad (17)$$

because, according to a well-known law, the one gas expands in the space just as if the second were not present; adding these two equations we get

$$Vp = (G_1 B_1 + G_2 B_2)(a + t), \quad . \quad . \quad . \quad (18)$$

where  $p$  equals the sum of the pressures  $p_1$  and  $p_2$ , which sum can be a matter of direct observation.

If  $v$  is the specific volume of the mixture, and  $G = G_1 + G_2$  its

total weight, then we have also  $V=Gv$ , and from the foregoing formulas there follows for the mixture

$$pv = \left( \frac{G_1 B_1 + G_2 B_2}{G_1 + G_2} \right) (a+t).$$

If we designate the coefficient of  $(a+t)$  in the right member by  $B_m$ , then, just as for a simple gas, we have for the mixture

$$pv = B_m(a+t),$$

for which the constant  $B_m$  is determined by

$$B_m = \frac{B_1 G_1 + G_2 B_2}{G_1 + G_2}. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

We at once recognize that this law is true for more than two gases, and that in such a case we get for the mixture the general relation

$$B_m = \frac{\Sigma(GB)}{\Sigma(G)}. \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

The pressures of the separate gases in the mixture are easily obtained if we divide equations (17) by equation (18); we then get respectively

$$\frac{p_1}{p} = \frac{G_1 B_1}{G_1 B_1 + G_2 B_2} \quad \text{and} \quad \frac{p_2}{p} = \frac{G_2 B_2}{G_1 B_1 + G_2 B_2}, \quad . \quad . \quad (20)$$

which proposition can easily be transferred to the case in which more than two gases are present.

If the constant  $B_m$  for a mixture of two gases has been determined by observation, then the proportions of the mixture can easily be determined from equation (19).

If the weight of the two gases is  $G=G_1+G_2$ , we have

$$\frac{G_2}{G} = 1 - \frac{G_1}{G},$$

and we can directly determine from equation (19)

$$\frac{G_1}{G} = \frac{B_m - B_2}{B_1 - B_2} \quad \text{and} \quad \frac{G_2}{G} = \frac{B_1 - B_m}{B_1 - B_2}. \quad . \quad . \quad . \quad (21)$$

If we utilize these two formulas in equation (20), we get the pressure  $p_1$  of the one gas and  $p_2$  of the other gas from the equations

$$\text{and } \left. \begin{aligned} \frac{p_1}{p} &= \frac{(B_m - B_2)B_1}{(B_1 - B_2)B_m} = \frac{G_1B_1}{GB_m} \\ \frac{p_2}{p} &= \frac{(B_1 - B_m)B_2}{(B_1 - B_2)B_m} = \frac{G_2B_2}{GB_m} \end{aligned} \right\} \dots \dots \dots (22)$$

The most important case of gas mixture is presented by atmospheric air, which is composed of nitrogen and oxygen<sup>1</sup>; for air, therefore, the foregoing values can easily be computed. According to the tabulation on page 104 we have for nitrogen  $B_1 = 30.131$  [54.920], for oxygen  $B_2 = 26.472$  [48.251], and for atmospheric air  $B_m = 29.269$  [53.349]. From equation (21) therefore follows, for air,

$$\frac{G_1}{G} = 0.7644 \quad \text{and} \quad \frac{G_2}{G} = 0.2356.$$

Accordingly atmospheric air is composed by weight of

76.44% nitrogen and 23.56% oxygen.

Equations (22) on the other hand give

$$\frac{p_1}{p} = 0.7869 \quad \text{and} \quad \frac{p_2}{p} = 0.2131.$$

At the pressure  $p$  of atmospheric air, corresponding, for example, to an observed reading of the barometer, we have 78.69%

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<sup>1</sup> Remark.—According to the recent investigations by Lord Rayleigh and William Ramsay atmospheric air does not consist solely of a mixture of oxygen and nitrogen, but also of other hitherto unknown gases, and each of them monatomic, which, as new chemical elements, have received the names Helium, Neon, Argon, Krypton, and Xenon; of these the first mentioned has been already subjected to a closer chemical and physical examination. This highly interesting discovery is one of the most important results which the production of liquid air has rendered possible. In the technical investigation of atmospheric air, only considered in the present treatise, we may neglect these tiny admixtures of other gases.

of the pressure due to nitrogen and 21.31% due to oxygen, provided the proportions of the mixture of atmospheric air are invariable and correspond exactly to the values just computed. According to recent investigations the proportion of our atmospheric mixture is subject to variations, to be sure between narrow limits; consequently the just computed pressure ratios vary somewhat; but concerning this variation no conclusion can be drawn from the observation of the total pressure  $p$ , that is, of the variable reading of the barometer.

Chemists usually compare gases by their *v o l u m e s* at the same pressure and the same temperature, and not by weights.

In the present case,  $G_1$  kg. [lbs.] of the one gas at the pressure  $p$  and the temperature  $t$  has the volume  $V_1$ , and the  $G_2$  kg. [lbs.] of the other gas would occupy the volume  $V_2$  at this pressure  $p$  and temperature  $t$ , and for these gases the relations would subsist:

$$V_1 p = G_1 B_1 (a + t) \quad \text{and} \quad V_2 p = G_2 B_2 (a + t);$$

and from the addition of the two equations, and because  $V_1 + V_2 = V$  represents the total volume, we would get

$$V p = (G_1 B_1 + G_2 B_2) (a + t),$$

and according to equation (19)

$$V p = G B_m (a + t).$$

If we use this as a divisor for the two preceding equations, we get the proportions of the mixture *b y v o l u m e*:

$$\frac{V_1}{V} = \frac{G_1 B_1}{G B_m} \quad \text{and} \quad \frac{V_2}{V} = \frac{G_2 B_2}{G B_m}. \quad . \quad . \quad . \quad . \quad (23)$$

But these expressions are identical with the pressure proportions of equation (22).

From these computations it follows, for example, that atmospheric air consists *b y v o l u m e* of 78.69% nitrogen and 21.31% oxygen.

If we can conceive the mixture to consist of any number of



As we must enter more fully into this question later on in the treatise, we will only briefly elucidate the first case. Let us assume

chemical combination of the elements . . .  $E_1 E_2 E_3 \dots$   
 of which the atomic weights are . . .  $e_1 e_2 e_3 \dots$   
 and furthermore let . . .  $n_1 n_2 n_3 \dots$

represent the number of atoms existing respectively in the elementary gases before the chemical combination is effected, then the molecular weights of the individual gases will be  $m_1 = n_1 e_1$ ,  $m_2 = n_2 e_2$ , etc., and these values will enter equation (24) in place of the weights  $G_1, G_2$ , etc.

We therefore have

$$\Sigma(G) = n_1 e_1 + n_2 e_2 + \dots = \Sigma(ne)$$

and

$$\sum \left( \frac{G}{\epsilon} \right) = \frac{n_1 e_1}{\epsilon_1} + \frac{n_2 e_2}{\epsilon_2} + \dots$$

Now for the elements the relative weights  $\epsilon$  (with respect to hydrogen) are identical with the atomic weights, consequently the last formula gives simply

$$\sum \left( \frac{G}{\epsilon} \right) = \Sigma(n),$$

and hence we have from equation (24) the relative weight  $\epsilon_m$  of the mixture

$$\epsilon_m = \frac{\Sigma(ne)}{\Sigma(n)}.$$

But  $\Sigma(ne)$  signifies the molecular weight  $m$  of the chemical combination in question, and  $\Sigma(n)$  is the number  $n$  of the atoms of which this consists; therefore the relative weight of the mixture is simply

$$\epsilon_m = \frac{m}{n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

while the relative weight  $\varepsilon$  of the corresponding chemical combination is

[illegible]

where  $m_0=2$  is the molecular weight of hydrogen. If  $v_m$  is the specific volume of the mixture and  $v$  that of the chemical combination, then, according to equation (3c), p. 102, we have for the same pressure and temperature the relation

$$v\varepsilon = v_m\varepsilon_m,$$

and from this follows with the utilization of the preceding values, putting  $m_0=2$ ,

$$\frac{v}{v_m} = \frac{\epsilon_m}{\epsilon} = \frac{2}{n}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (27)$$

From this we can draw the conclusion as to the change of volume when the mixture is converted by ignition, or by simply heating, into a chemical combination, provided that at the end the initial pressure and the initial temperature are again restored.

Moreover, constant  $B$  of the equation of condition can be found from equation (11):

for the mixture  $B_m = n \frac{B_0}{m}$ ,

for the chemical combination  $B=2\frac{B_0}{m}$ ;

of course it is here assumed that the chemical combination in a state of vapor obeys the equation of condition of gases. In diatomic gases, for which  $n=2$ , no change of volume occurs, as equation (27) shows. When a union of nitrogen and oxygen takes place in the proportions corresponding to the chemical compound nitric oxide (NO) we have the value of  $B$  the same for the mechanical mixture as for the chemical combination.

By weight, moreover, the mixture is composed as follows:

$$\frac{G_1}{G} = \frac{n_1}{m} e_1; \quad \frac{G_2}{G} = \frac{n_2}{m} e_2; \quad \frac{G_3}{G} = \frac{n_3}{m} e_3. \quad \cdot \quad \cdot \quad \cdot \quad (28)$$

By volume, on the other hand, it is composed as per equations (23), when we consider that, according to equation (11),



$B_0 = B_1 \epsilon_1$ ,  $B_0 = B_2 \epsilon_2$ , etc., also  $B_0 = B_m \epsilon_m$ , and we have besides  $e_1 = \epsilon_1$ ,  $e_2 = \epsilon_2$ , etc.; then

$$\frac{V_1}{V} = \frac{n_1}{m} \epsilon_m; \quad \frac{V_2}{V} = \frac{n_2}{m} \epsilon_m; \quad \frac{V_3}{V} = \frac{n_3}{m} \epsilon_m. \quad . \quad . \quad . \quad (29)$$

These last expressions at the same time indicate, as comparison of equation (23) with equations (22) shows, in what proportion the individual gases contribute in the way of pressure to the total pressure  $p$  of the mixture; we therefore also have

$$\frac{p_1}{p} = \frac{n_1}{m} \epsilon_m; \quad \frac{p_2}{p} = \frac{n_2}{m} \epsilon_m; \quad \frac{p_3}{p} = \frac{n_3}{m} \epsilon_m. \quad . \quad . \quad . \quad (30)$$

Thus we have, say, for a mixture of hydrogen and oxygen in the proportions necessary to form water, that is, for the so-called detonating gas, the relative weight of this gas  $\epsilon_m = 6$ , according to equation (25), and that of the vapor of water (considered to be highly superheated) after explosion to be  $\epsilon = 9$ , because, according to the chemical formula of water,  $H_2O$ , the number of atoms  $n = 3$  and the molecular weight of the water is

$$m = n_1 e_1 + n_2 e_2 = 2 \times 1 + 1 \times 16 = 18.$$

The constant  $B$  of the equation of condition for detonating gas is

$$B_m = \frac{B_0}{6} = \frac{422.591}{6} = 70.432 \quad \left[ \frac{770.259}{6} = 128.377 \right];$$

and that for the vapor of water, of course considered in the state in which it can be regarded as a gas, is

$$B = \frac{B_0}{9} = 46.954 \quad \left[ \frac{770.259}{9} = 85.584 \right].$$

The ratio of the volumes of this steam and of the detonating gas is, according to equation (27),

$$\frac{V}{V_m} = \frac{2}{3};$$

therefore a marked reduction of volume is connected with the explosion, provided the product is brought back to the same pressure and the same temperature.

The mixture (detonating gas) and also this vapor of water are, according to equation (28), composed by weight as follows:

$$\frac{G_1}{G} = \frac{n_1}{m} e_1 = \frac{2}{18} \times 1 = \frac{1}{9}; \quad \frac{G_2}{G} = \frac{n_2}{m} e_2 = \frac{1}{18} \times 16 = \frac{8}{9}.$$

On the other hand the composition of the mixture (detonating gas) by volume, according to equation (29), is

$$\frac{V_1}{V} = \frac{n_1}{m} \epsilon_m = \frac{2}{18} \times 6 = \frac{2}{3}$$

and 
$$\frac{V_2}{V} = \frac{n_2}{m} \epsilon_m = \frac{1}{18} \times 6 = \frac{1}{3}.$$

The same values exist for the pressure proportions. If  $p$  is the pressure of the mixture, then the pressure of the hydrogen is  $p_1 = \frac{2}{3}p$ , and that of the oxygen is  $p_2 = \frac{1}{3}p$ .

In the same way we can find for ammonia,  $\text{NH}_3$ , the number of atoms to be  $n=4$ , and the molecular weight  $m=17$ . This compound is of technical importance because of its application in refrigerating machines. For the mixture of nitrogen and hydrogen in the corresponding proportions we have  $\epsilon_m=17/4$ , and for the chemical compound in the form of ammonia we have  $\epsilon=17/2$ ; the volumetric ratio between this steam and the mixture is

$$\frac{v}{v_m} = \frac{1}{2}.$$

The constant of the equation of condition for the mixture is  $B_m=99.432$  [181.24], and for the vapor of ammonia (highly superheated)  $B=49.716$  [90.618]. By weight the mixture consists of 14/17 nitrogen and 3/17 hydrogen; on the other hand, by volume it consists of 1/4 nitrogen and 3/4 hydrogen; the pressures of the two elementary gases in the mixture likewise possess the same ratio to each other.

It deserves to be emphasized that the just calculated values of  $B$  for the vapors of water and of ammonia have no technical value. These vapors, considered as subject to the equation of condition for gases, show too great deviations within the limits for which they are employed. In the investigations concerning the behavior of vapors we will return to this question.

## § 21. SPECIFIC HEAT OF GASES.

The quantity of heat which is necessary to raise one kilogram [1 lb.] of water from  $0^{\circ}$  C. [ $32^{\circ}$  F.] to  $1^{\circ}$  C. [ $33^{\circ}$  F.] is the unit of heat and constitutes the unit for heat measurement (it is known as the calorie in the French system of units, and as the British thermal unit in the English system); the quantity of heat  $dQ$  needed to heat water from  $0^{\circ}$  C. [ $32^{\circ}$  F.] an amount  $dt$  is therefore  $dQ = dt$ .

In order to heat a unit of weight of any other body from any initial temperature  $t$  an amount  $dt$  (and here we will consider solid or fluid bodies), the quantity of heat needed will be different and is simply written as

$$dQ = c dt, \quad . . . . . (31)$$

here assuming that for the body in question the factor  $c$  is determined by experiment. The value  $c$  is called the specific heat of this body, and therefore represents the ratio

$$c = \frac{dQ}{dt},$$

namely, the ratio of the quantity of heat which the body absorbs for a change of temperature  $dt$  compared with that needed by an equal mass of water for the same rise of temperature; in so doing, however, it is expressly understood that the water has the initial temperature  $0^{\circ}$  C. [ $32^{\circ}$  F.], for which condition  $c=1$ , while the body in question has for the initial temperature any value of  $t$  (but assumed as known), because experiments have shown the specific heat  $c$  to vary with the temperature, that is, have shown  $c$  to be a function of  $t$ . This variability with the initial tempera-

ture is also manifested by water. This is the reason that in the above comparison water was taken at the initial temperature of  $0^{\circ}\text{C}$ . [ $32^{\circ}\text{F}$ .], for thus only can a reliable basis for comparison be established.

We have just compared the unit of weight of a body with the unit of weight of water, and therefore  $c$  is also called the specific heat for equal weight or weight capacity.

We might also have taken a cubic unit, cubic meter [cu. ft.], of the body and compared it with a cubic unit of water at  $0^{\circ}\text{C}$ . [ $32^{\circ}\text{F}$ .] with respect to its heat absorption for the increment of temperature  $dt$ , and then we would be dealing with specific heat for equal volume, or volume capacity.

But the one kind of specific heat can easily be determined from the other.

Let  $\gamma$  be the specific weight of the body, i.e., the weight of a cu. meter of the body measured in kg. [the weight of a cu. ft. of the body measured in lbs.], and if  $\gamma_0$  is the specific weight of water ( $\gamma_0=1000$ ) [ $\gamma_0=62.425$ ], then the body will need the quantity of heat  $\gamma\,cdt$  for the rise of temperature  $dt$ , and the water will need the quantity of heat  $\gamma_0 dt$  starting from  $0^{\circ}\text{C}$ . [ $32^{\circ}\text{F}$ .]; the ratio  $\omega$  of the two is therefore

$$\omega = \frac{\gamma}{\gamma_0} c, \quad . . . . . (32)$$

and that is the specific heat for equal volumes; it is obtained by multiplying the specific heat  $c$ , for equal weight, by the quotient  $\gamma : \gamma_0$ , i.e., by the relative weight of the body with respect to water.

The foregoing presentation of the older works on Physics must, however, be extended according to the theory of Thermodynamics, for the quantity of heat needed by the body for the temperature rise  $dt$  is by no means solely dependent on this rise and on its initial temperature. The temperature is a function of the pressure and volume of the body, and as the body experiences a change of volume, while it is receiving heat under the external pressure  $p$ ,

there must be considered here the external work performed by, or expended on, the body. In Section I, § 3, p. 27, it was distinctly explained that the quantity of heat which can be imparted for a certain change of state depends upon the path along which the body is passed from the initial to the given final condition, and that there must be an infinite number of such passages, and equation (31) has therefore, in principle, no general validity, but presupposes in its application a perfectly definite law of change of the external pressure  $p$  with the volume  $v$  of the body. For gases this law will appear in subsequent developments; but for every other relation between  $p$  and  $v$  during heat supply equation (31) will have no meaning. It is so with solid and liquid bodies, only with the difference that for such bodies the general law of the changes of state for which equation (31) is true is not even known, because the so-called equation of condition of solid and liquid bodies has not yet been found; this much can be regarded as certain, that equation (31) can only be used with such solid and liquid bodies as experience during heating an imperceptible change of volume, which can be neglected in the computations, because in this case the outer work is of no account. With gases, heating is in general accompanied with considerable changes of volume, and therefore from the beginning the difference could not be disregarded; consequently even before the question was clarified by Thermodynamics two kinds of heating of gases were distinguished from each other; the heating of the gas was considered as taking place under constant pressure or under constant volume; in the first case let the quantity of heat for the rise of temperature  $dt$  of the gas be

$$dQ_p = c_p dt, \quad . . . . . (33)$$

and, in the other case, let

$$dQ_v = c_v dt, \quad . . . . . (34)$$

where the subscript  $p$  or  $v$  indicates which magnitude is supposed to be constant during the heat supply considered.

We call  $c_p$  the specific heat of the gas under constant pressure, and  $c_v$  that under constant volume, and really we ought to add, in both cases, for equal

weight, as a kg. [lb.] of the gas was compared with a kg. [lb.] of the water; but this supplementary remark is unnecessary, for in all Thermodynamic investigations the unit weight of the bodies in question is assumed, and it is only in exceptional cases that the unit of volume is considered.

Moreover the two cases of heating of the gas just mentioned will in the future investigations appear as only special cases of a general law; but for the questions to be treated here these two cases are of marked significance, because the values  $c_p$  and  $c_v$  for the different gases have been determined by experiment.

The first reliable experiments with respect to the value  $c_p$ , the specific heat of gases under constant pressure, we again owe to Regnault.<sup>1</sup> The following tabulation gives the values of  $c_p$  and of the product  $\gamma c_p$ , where  $\gamma$  is the specific weight, that is, the weight of a cubic unit of the gas (see p. 103) for those particular gases which obey sufficiently closely the above equation of condition. If we divide the latter product  $\gamma c_p$  by the specific weight  $\gamma_0 = 1000$  [ $\gamma_0 = 62.423$ ], we get for the corresponding gas, as was already explained, the specific heat under constant pressure for equal volumes.

	$c_p$ .	French $\gamma c_p$ .	English $\gamma c_p$ .
Atmospheric Air.....	0.2375	0.3071	0.01917
Hydrogen.....	3.4090	0.3053	0.01906
Oxygen.....	0.2175	0.3110	0.01941
Nitrogen.....	0.2438	0.3062	0.01912
Nitric Oxide.....	0.2317	0.3114	0.01942
Carbonic Oxide.....	0.2450	0.3065	0.01913

We see that the specific weight  $c_p$  is different for the different gases, but that hydrogen stands out in a remarkable fashion; its specific heat is, as other experiments also show, even greater than for any solid or liquid body.

It is different with the values  $\gamma c_p$  of the last column, which are nearly equal for the given gases, as was early recognized by Delaroche and Bérard; the smallest value appears with hydrogen, and as this gas, according to experience, stands near

<sup>1</sup> Rel. II, 303.

est to the perfect gas, we conclude, in accordance with the supposition under which the equation of condition was derived, that any individual gas deviates more from these suppositions the greater the deviation of its value  $\gamma c_p$  from that belonging to hydrogen. But for the gases just adduced the deviations are so insignificant that for this reason also we can utilize the equation of condition with all of them. If we assume complete equality of the values  $\gamma c_p$ , then we may conclude that for equal volumes all gases require the same quantity of heat for the same rise of temperature under constant pressure, which proposition, according to Avogadro's law, § 19, p. 107, can also be extended to the molecules themselves.

But the investigations of Regnault concerning the specific heat of gases under constant pressure have led to still other results which are important for the discussions which are to follow.

First of all, his extended experiments show that for atmospheric air, hydrogen, and carbonic acid the specific heat is independent of the pressure, and that therefore the unit of weight of every one of these gases needs always the same quantity of heat for the rise of temperature  $dt$  under a constant but arbitrary pressure, whatever the volume may happen to be; this is true even of carbonic acid, which in other respects by no means obeys the equation of condition of gases. Furthermore it has been shown that for atmospheric air and hydrogen the specific heat  $c_p$  is a constant quantity between wide temperature limits ( $-30^\circ \text{C.}$  to  $200^\circ \text{C.}$ ) [ $-22^\circ \text{F.}$  to  $392^\circ \text{F.}$ ]. On the other hand the specific heat of carbonic acid grows not inconsiderably with rising temperatures. From this the conclusion has been drawn that for the gases mentioned in the above tabulations and which were formerly designated as the permanent gases, the specific heat under constant pressure within the ordinary pressure and temperature limits (which alone are to be considered for the present), may be regarded as independent of the pressure and temperature, and therefore considered as a constant value. But for high pressure and for high temperature, even for low temperatures at which

the gas approaches the liquid condition, we must give up this assumption.

So far as the specific heat of gases under constant volume ( $c_v$ ) is concerned, no direct determination has yet been successfully made, but by different experimental methods the ratio

$$\kappa = \frac{c_p}{c_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

of the specific heats  $c_p$  and  $c_v$  has been determined; the most important of these methods we will discuss more fully later on.

According to the formula given by Laplace for the velocity of sound which contains this value  $\kappa$ , there was determined for  $\kappa$  on the average 1.403; for the velocity of sound is accurately known in air. Dulong found from experiments of the oscillations of gases in pipes, for atmospheric air  $\kappa=1.421$ , for carbonic oxide  $\kappa=1.428$ , and for carbonic acid 1.338, but then these experiments show certain imperfections.

More exact experiments of a similar sort, using the procedure given by Kundt, are due to Wüllner, who deserves the credit of taking account at the same time of the influence of the temperature. Among other results Wüllner found corresponding temperatures of 0° C. [32° F.] to 100° C. [212° F.] for atmospheric air  $\kappa=1.4053$  and 1.4029 respectively, and also for carbonic acid he found  $\kappa=1.4032$  and 1.3946 respectively.

According to other experimental methods, differing but little from each other in principle and which will be touched upon later in this treatise, there was found for atmospheric air by Clément 1.356, by Masson 1.419, by Hirn 1.384, by Weisbach 1.402, by Cazin 1.410, and by Röntgen 1.405.

Other careful and recent experiments by Lummer and Pringsheim have given for atmospheric air  $\kappa=1.4015$ , for hydrogen 1.4084, for oxygen 1.3962, and for carbonic acid 1.2961. As a mean value we will hereafter take

$$\kappa = 1.410,$$



and will assume that this magnitude, as well as  $c_p$ , is independent of temperature and pressure under ordinary conditions. Then, according to equation (35), the specific heat  $c_v$  under constant volume becomes constant. For atmospheric air, the technically most important gas, there is given  $c_p=0.2375$ ; consequently when  $\kappa=1.410$  there follows  $c_v=0.1684$ .

## § 22. FIRST FUNDAMENTAL EQUATION OF THERMODYNAMICS WITH RESPECT TO GASES.

The quantity of heat  $dQ$  which is to be imparted to a unit of weight of a body in order to increase its pressure, volume, and temperature by  $dp$ ,  $dv$ , and  $dt$  respectively, was given by equations (IIIa), § 12, p. 62:

$$\left. \begin{aligned} dQ &= A[X dp + Y dv] \\ &= \frac{A}{\frac{\partial t}{\partial p}} [X dt + T dv] \\ &= \frac{A}{\frac{\partial t}{\partial v}} [Y dt - T dp] \end{aligned} \right\} \dots \dots \dots (36)$$

In these three identical equations  $T$  means the C a r n o t function of temperature whose form for the present is still unknown; the two magnitudes  $X$  and  $Y$  are functions of  $p$  and  $v$  for the body in question, and it is these magnitudes which we must now ascertain for gases.

If for one case we assume the body to be heated under constant pressure and in another case under constant volume, then the third of these fundamental equations gives for the first case (for  $dv=0$ )

$$dQ_p = \frac{AY}{\frac{\partial t}{\partial v}} dt, \dots \dots \dots (37)$$

and the second equation, for  $dv=0$ , gives

$$dQ_v = \frac{AX}{\frac{\partial t}{\partial p}} dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

A comparison of these two formulas with equations (33) and (34) now furnishes

$$AY = c_p \frac{\partial t}{\partial v} \quad \text{and} \quad AX = c_v \frac{\partial t}{\partial p}. \quad . \quad . \quad . \quad . \quad (39)$$

Both formulas are still valid for every body, and from what has preceded we can, especially for gases, consider the specific heats  $c_p$  and  $c_v$  to be constant, and, from the equation of condition

$$pv = B(a+t) \\ [pv = B(a+t-32^\circ)],$$

there follows, by differentiation,

$$\frac{\partial t}{\partial v} = \frac{p}{B} \quad \text{and} \quad \frac{\partial t}{\partial p} = \frac{v}{B}, \quad . \quad . \quad . \quad . \quad (40)$$

and by substitution in equation (39) we get

$$Y = \frac{c_p}{AB} \cdot p \quad \text{and} \quad X = \frac{c_v}{AB} \cdot v. \quad . \quad . \quad . \quad . \quad (41)$$

From this we see that for gases the function  $Y$  is only dependent on  $p$  and the function  $X$  only on  $v$ , and furthermore that these functions are directly proportional to the corresponding values.

Now the first fundamental equation of Thermodynamics, according to equation (Ia), § 12, p. 62, has the form

$$\frac{\partial Y}{\partial p} - \frac{\partial X}{\partial v} = 1.$$

The differentiation of equations (41) and the substitution of the two different coefficients in the preceding equation then give

$$c_p - c_v = AB \quad . \quad . \quad . \quad . \quad . \quad (42)$$

as the form into which the first fundamental equation passes when applied to gases. If we here use the symbols given in equation (35), we get the following forms:

$$c_p - c_v = c_v(\kappa - 1) = c_p \frac{\kappa - 1}{\kappa} = AB, \quad . \quad . \quad . \quad . \quad (43)$$

and according to equations (41) the formulas for the two functions  $X$  and  $Y$  take the simpler form

$$Y = \frac{\kappa p}{\kappa - 1} \quad \text{and} \quad X = \frac{v}{\kappa - 1}. \quad . \quad . \quad . \quad . \quad (44)$$

The important equation (42) was first given in this form by *Clausius*; it contains four magnitudes, every one of which was determined by special experiments; the substitution in this equation of the experimentally determined quantities must give the corresponding connection. Thus if we substitute for atmospheric air the above-given values  $c_p = 0.2375$ ,  $B = 29.269$  [53.349], and  $A = 1:424$  [1:772.83], then the formula becomes  $c_v = 0.1685$  and consequently  $\kappa = 1.4095$ , or in round numbers  $\kappa = 1.410$ , in agreement with the data<sup>1</sup> given in the preceding paragraph.

If we hold fast to *Regnault's* assumptions for  $B$  and  $c_p$  for air, and take  $\kappa = 1.4015$  according to *Lummer* and *Pringsheim*, then according to equation (43) the mechanical equivalent 1:A has the value 430.18 [784.09], which value agrees with that given by *Dietrich*. From this we can conclude that a later determination of the mechanical equivalent of heat, completely free of all objections, will lead to a somewhat greater value than (424) [772.83] given by *Joule*, the value which we will still continue to assume for the present.

Computing  $c$  in the same way from equation (42), the following table gives, in the first column, for the gases already enumerated, the specific heat at constant volume

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<sup>1</sup> If we pursue the line of thought of *Robert Mayer* (1842), who first computed the mechanical equivalent of heat, it will be found to correspond, when brought into mathematical form, to equation (42) of the text; although *Mayer* found 365 instead of 424, this must be ascribed to the fact that, following *Bérard*, he took the specific heat  $c_p$  of air as equal to 0.267, while the true value  $c_p = 0.2375$  was not found until later by *Regnault*.

for equal weights; while in the second column are placed the products  $\gamma c_v$ , which are found with the help of the values  $\gamma$  given in table on p. 104; dividing these products  $\gamma c_v$  by  $1 \times 1000$  [ $1 \times 62.425$ ] will give, for equal volumes of the different bodies, the specific heat at constant volume.

	$c_v$ .	French $\gamma c_v$ .	English $\gamma c_v$ .
Atmospheric Air.....	0.1685	0.2170	0.01360
Hydrogen.....	2.4123	0.2161	0.01349
Oxygen.....	0.1551	0.2217	0.01384
Nitrogen.....	0.1727	0.2169	0.01354
Nitric Oxide.....	0.1652	0.2218	0.01385
Carbonic Oxide.....	0.1736	0.2172	0.01356

We see from the values of the 2d [and 3d] columns that the specific heat  $c_v$ , taken at equal volumes, is nearly the same for all gases; we conclude from this that all gases require the same quantity of heat for the same rise in temperature, provided the unit of volume is used in the experiment; this is also the case with the specific heat under constant pressure, and was discussed in connection with the table on p. 119.

If we introduce into the following formulas the weight  $\epsilon$  of the gas relatively to hydrogen, as was done in § 19 when discussing the equation of condition, there results a series of simple propositions which are worth emphasizing. Multiplying both members of equation (42) by  $\epsilon$ , we get

$$\epsilon(c_p - c_v) = AB\epsilon.$$

Because of the relation  $B_0 = B\epsilon$  of equation (11), where  $B_0 = 422.591$  [770.259] is the constant  $B$  for hydrogen belonging to the equation of condition (see Table p. 104), there follows

$$\epsilon(c_p - c_v) = AB_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

according to which the left member of the equation is a constant quantity for all gases, a point to which Clapeyron<sup>1</sup> had already called attention. Moreover the value of  $AB_0$ , as was incidentally noted with equation (12) in § 19, p. 104, is so nearly

<sup>1</sup> Poggendorff's Annalen, Vol. 59, p. 451 (1843).

equal to unity (or, more exactly,  $AB_0=0.9967$ , for the values of the constants  $A$  and  $B_0$  used in this book) that in most computations use can be made of the assumption  $AB_0=1$ , but as there is so far no theoretical justification for this relation, no use will be made of it in the course of this book.

Because in the gases quoted the relative weight  $\varepsilon$  is identical with half the molecular weight  $m$  we can also write equation (45) in the form

$$m(c_p - c_v) = 2AB_0 = 1.9934. \quad . \quad . \quad . \quad . \quad (46)$$

For a mechanical mixture of gases equation (24) gave

$$\varepsilon_m = \frac{\Sigma(G)}{\Sigma\left(\frac{G}{\varepsilon}\right)},$$

where  $G_1, G_2, G_3, \dots$  are the weights of the individual gases and  $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots$  their relative weights with respect to hydrogen; consequently for the unit of weight of such a mixture equation (45) gives

$$c_p' - c_v' = AB_0 \Sigma\left(\frac{G}{\varepsilon}\right), \quad . \quad . \quad . \quad . \quad . \quad (47)$$

if its specific heats are designated by  $c_p'$  and  $c_v'$ , or, if we substitute the molecular weights of the gases,

$$c_p' - c_v' = 2AB_0 \Sigma\left(\frac{G}{m}\right). \quad . \quad . \quad . \quad . \quad . \quad (48)$$

For those mixtures which consist of simple gases having  $\kappa=1.410$  this value of  $\kappa$  belongs also to the mixture itself, and consequently

$$c_v' = \frac{2AB_0}{\kappa - 1} \Sigma\left(\frac{G}{m}\right) = 4.8618 \times \Sigma\left(\frac{G}{m}\right).$$

For example, atmospheric air consists of  $G_1=0.7644$  kg. [lb.] nitrogen,  $G_2=0.2356$  kg. [lb.] oxygen, and  $m_1=28, m_2=32$ ; therefore for air we have, according to the last formula,

$$c_v' = 0.1685,$$

which agrees with the value found before.

In cases like the foregoing it is best to first compute the relative weight  $\epsilon_m$  of the mixture, then, by equation (45),

$$\epsilon_m(c_p' - c_v') = AB_0, \quad . \quad . \quad . \quad . \quad . \quad (48a)$$

and from this find  $c_p' - c_v'$ ; from this difference and for the case when the mixture is composed of simple gases,  $\kappa = 1.410$ , the values  $c_v'$  and  $c_p'$  can be computed separately, as was done in the preceding example.

For the special case in which the constituent gases are mixed in such a ratio as to permit of a chemical combination, we get for the latter

$$\epsilon(c_p - c_v) = AB_0;$$

consequently there exists between chemical combination and mechanical mixture the relation

$$\epsilon(c_p - c_v) = \epsilon_m(c_p' - c_v'), \quad . \quad . \quad . \quad . \quad . \quad (48b)$$

or, if we utilize equations (25) and (26), we have from equation (48a)

$$c_p' - c_v' = \frac{AB_0}{m} \times n, \quad . \quad . \quad . \quad . \quad . \quad (49a)$$

and from equation (48b)

$$c_p - c_v = \frac{2}{n}(c_p' - c_v'), \quad . \quad . \quad . \quad . \quad . \quad (49b)$$

where  $m$  represents the molecular weight of the combination and  $n$  the number of atoms.

For example, the mixture of hydrogen and oxygen known as detonating gas, which becomes steam when chemically combined, has  $m = 18$  and  $n = 3$  (see p. 105). Consequently for detonating gas  $c_p' - c_v' = 0.1667$ , and for steam  $c_p - c_v = 0.1111$ . For detonating gas  $\kappa = 1.410$ , and therefore this gas has  $c_v' = 0.4066$  and  $c_p' = 0.5733$ ; on the other hand the values  $c_p$  and  $c_v$  cannot be computed for steam (supposed to be in the gaseous condition) because their ratio is unknown. To be sure Regnault did find for steam  $c_p = 0.4805$ , and accordingly  $c_v = 0.3694$ ; but the experimental result was for steam near the

point of condensation; there will be opportunity later to follow up more fully this also technically important problem.

To bring up another example, let us consider ammonia; for it and the corresponding mechanical mixture (see p. 105)  $m=17$  and  $n=4$ ; therefore, according to equations (49a and b),

$$\begin{aligned}c_p' - c_v' &= 0.2345 \text{ for the mixture,} \\ c_p - c_v &= 0.1172 \text{ for ammonia vapor.}\end{aligned}$$

As the mixture consists of simple gases, we have for them again  $\kappa=1.410$  and therefore

$$c_p' = 0.8064; \quad c_v' = 0.5719. .$$

### § 23. SECOND FUNDAMENTAL EQUATION OF THERMODYNAMICS WITH RESPECT TO THE BEHAVIOR OF GASES.—DETERMINATION OF THE CARNOT FUNCTION.

According to equation (IIa), p. 62, the second fundamental equation is perfectly general for every body and has the following form

$$Y \frac{\partial t}{\partial p} - X \frac{\partial t}{\partial v} = T;$$

in this  $T$  is a function of the temperature  $t$  about which it is only known that it must have the same form for all bodies in Nature; concerning the form itself, however, the former general investigations give no clue.

If we substitute in the foregoing equations the values of  $Y$  and  $X$  found for gases by equations (44), namely,

$$Y = \frac{\kappa p}{\kappa - 1} \quad \text{and} \quad X = \frac{v}{\kappa - 1},$$

and if we also replace both the differential coefficients by equation (40), as it was found for gases, namely,

$$\frac{\partial t}{\partial p} = \frac{v}{B} \quad \text{and} \quad \frac{\partial t}{\partial v} = \frac{p}{B},$$

then the foregoing fundamental equation can be written

$$T = \frac{\kappa p}{\kappa - 1} \frac{v}{B} - \frac{v \bullet p}{\kappa - 1} \frac{p}{B'}$$

or simply

$$T = \frac{pv}{R},$$

or, drawing on the equation of condition for gases (3a), p. 96,

$$T=a+t=273+t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{II}b)$$

$$[T = 491.4 + (t - 32) = 459.4 + t],$$

a result that is highly important for thermodynamics. The Carnot temperature function is therefore nothing but the absolute temperature, consequently it is the temperature of the body according to Celsius [Fahrenheit], measured from a point  $273^{\circ}$  [ $491.4^{\circ}$ ] below the freezing-point of water. Henceforth in this treatise the term "Carnot function" will no longer occur, but we will simply speak of the absolute temperature of a body; the equation of condition will be merely written in the form

$$pv = BT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

and the rise of temperature  $dt$  will as a rule be expressed as  $dT$ .

It has been repeatedly pointed out in this treatise, and first of all when the C a r n o t function was introduced into the general discussions of the first section, that not only the form but also the value of this function must be the same for all bodies possessing the same temperature; it is therefore sufficient to determine the relation for one kind of body, and now gases furnish us with the means of so doing; it alters nothing in the complete reliability of the declaration of equation (II*b*) that, strictly speaking, only hydrogen follows the law of M a r i o t t e and G a y - L u s s a c, and this gas only within certain limits; we have simply to consider as applying to this one body all



the considerations which preceded the derivation of equation (IIb).<sup>1</sup>

The establishing of the C a r n o t function now leads immediately to the function  $S=f(p, v)$ , which was introduced in the first section of this treatise (p. 31), and which was also shown, in the subsequent discussions, to be a function of temperature (see p. 60).

According to equation (43), p. 61, there results the relation

$$\frac{dS}{S} = \frac{dt}{T}$$

Now, according to the preceding, we here substitute  $T=a+t$ , then integration gives

$$S=k(a+t),$$

where  $k$  means an arbitrary constant of integration for which we can substitute unity. (Compare the remark upon p. 33.)

The further important result follows that function  $S$  is iden-

<sup>1</sup>Evaluation of the C a r n o t function for several temperature values was first attempted by C l a p e y r o n (ibid., 1834) by a clever utilization of different, and at that time somewhat uncertain, results of experimental investigations on gases and vapors. The temperature function designated by him with the letter  $C$  is connected with the symbol used in the text above by the relation  $C=AT$ ; from this follows by differentiation  $\frac{dC}{dt}=A=0.002358$ . For this differential coefficient C l a p e y r o n found on the basis of certain experiments the value 0.00187, and from another experimental series 0.002565, and calls attention to the slight difference of these values from each other, and concludes that  $C$  grows but slowly with the temperature. C l a p e y r o n then computed for five different temperatures lying between  $0^\circ$  and  $156.8^\circ$  the reciprocal value of  $C$  by two different methods, of which one gave a value which would have agreed almost exactly with the correct value if C l a p e y r o n had not used for the reciprocal value of the constant of expansion of gases the then known value 267 (instead of 273).

The form of the C a r n o t function was really first recognized by H e l m h o l t z ("Über die Erhaltung der Kraft," Berlin, 1847, p. 36), for he put the equation which was first developed by H o l t z m a n n ("Über die Wärme and Elastizität der Gase," Mannheim, 1845) with one of the equations of C l a p e y r o n (the second fundamental equation). At that time H e l m h o l t z did not pursue the question any further.

Clausius, in his first paper (1850), gave the C a r n o t function exactly in the form  $C=A(a+t)$ .

tical with the C a r n o t function  $T$ , and must therefore likewise be measured by the a b s o l u t e t e m p e r a t u r e.

Consequently in all formulas of the first section the function  $S$  can be replaced by the absolute temperature, and particularly the propositions there developed concerning the "transformation of pressure-curve and indicator diagrams," § 14, p. 69, now receive a simple interpretation.

If we write the function  $S$  as a function of  $p$  and  $v$ , we get

$$f(p, v) = T,$$

which equation passes into the form of the equation of condition (50), p. 129, but of course only for gases, namely,

$$pv = BT,$$

for all other bodies  $f(p, v)$  possesses another form and, incidentally it may be remarked, a still unknown form.

## § 24. THE ENERGY OR INNER WORK OF GASES.

At the very beginning of the general investigations of the first section, the function  $U = F(p, v)$  (equations 3 and 4, pp. 26 and 27) was introduced into the discussion and treated as the inner work of the body. The differential was written in the form

$$dU = X dp + Z dv.$$

The function  $Y$ , whose meaning for gases has already been recognized in eq. (41), p. 123, bears to the partial differential  $Z$  the relation  $Z = Y - p$ , according to equation 12, p. 32; therefore if we utilize the first of these equations (44) and at the same time reproduce the other of these equations, we have, specially for gases,

$$Z = \frac{p}{\kappa - 1} \quad \text{and} \quad X = \frac{v}{\kappa - 1}.$$

Substitution in the preceding formula for  $dU$  therefore gives

$$dU = \frac{1}{\kappa - 1}(vdp + pdv),$$

or simply

$$dU = \frac{d(pv)}{\kappa - 1}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

by integration we have

$$U = U_0 + \frac{pv}{\kappa - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

if we regard  $U_0$  as the constant of integration, and then the form of the function  $U = F(p, v)$  is determined for gases. The absolute value of the constant  $U_0$  is not determinable, and possibly may be different for different gases, provided in considering it we start with the same initial values, say, of the pressure, the volume, or of the temperature. For the greater part of all physical and technical investigations of gases the knowledge of the constant  $U_0$  is not necessary, because in the ordinary case of application of equation (52) the magnitude  $U_0$  disappears from the formulas.

If in the preceding equations we replace  $pv$  by  $BT$  and multiply both sides by  $A$ , we get

$$AdU = \frac{AB}{\kappa - 1} dT$$

and

$$AU = AU_0 + \frac{ABT}{\kappa - 1},$$

or if we use one of the relations of equation (43), p. 124,

$$AdU = c_v dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51a)$$

and

$$AU = AU_0 + c_v T. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52a)$$

In the latter formula  $AU$  means the energy measured in units of heat for which we will hereafter use the simple designation  $AU = J$ , and also  $AU_0 = J_0$ ; as a result we shall have

$$dJ = c_v dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51b)$$

and

$$J = J_0 + c_v T. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52b)$$

The magnitude  $J$  can be designated as the "heat-contents" of the unit of weight of gas at the (absolute) temperature  $T$ .

It is noteworthy that  $J$ , like  $AU$ , depends only on the temperature  $T$  whatever the pressure  $p$  or the volume  $v$  of the unit

of weight of the gas may be. If we imagine gas of a particular temperature  $T_1$  to be brought in any way to the temperature  $T$ , there will follow, according to equation (52b),

$$J - J_1 = c_v(T - T_1),$$

and this magnitude represents that part of the quantity of heat, supplied from the outside during this change, which has remained behind in the gas itself and has therefore been consumed in augmenting the heat-contents. In the following discussions, moreover, we will use the term "gas heat" in place of the expression "heat-contents" of a gas.

The thought lies nigh that at the absolute zero, therefore for  $T=0$ , we cannot properly speak of the heat-contents, and that therefore in equations (52a) and (52b) we may put either  $AU_0$  or  $J_0$  equal to zero.

In most cases there is no objection to such an assumption and the corresponding simplification of the two equations; nevertheless it is advisable to avoid the simplification, for it must be remembered that both equations were derived from observations on gases which, after all, were limited to a comparatively narrow range of temperature values. Of course in gases, and also in all other bodies, the assumption is permissible that at the absolute zero there exists such a complete decomposition and scattering of the body that its smallest parts have passed completely out of the sphere of mutual force interactions, and have also passed into a state of rest.

## § 25. THE HEAT EQUATIONS AND THE ENTROPY OF GASES.

If we utilize the foregoing results for the transformation of the general equations (IIIa), p. 62, presented in the first section, we now get, especially for gases, the fourth of the formulas there adduced with the help of equation (51) or (51a),

$$dQ = \frac{A}{\kappa - 1} d(pv) + A p dv \quad . \quad . \quad . \quad . \quad (53a)$$

and

$$dQ = c_v dT + A p dv. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53b)$$

On the other hand the transformation of the first three of equations (IIIa) gives, as can easily be seen when we utilize formulas (40), (43), and (44), p. 123 and 124, the set

$$dQ = \frac{A}{\kappa - 1} (v dp + \kappa p dv) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53c)$$

$$= c_v \left( dT + (\kappa - 1) T \frac{dv}{v} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53d)$$

$$= c_p \left( dT - \frac{\kappa - 1}{\kappa} T \frac{dp}{p} \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53e)$$

and it is in this form that the equations will be now applied to gases; the different formulas are identical, and in solving particular problems that one is picked out which evidently leads most quickly to the goal; as a rule, in doing this, the equation of condition will be employed in one of the following forms, resulting from the combination of equation (50) with equation (43), p. 124:

$$A p v = A B T = c_v (\kappa - 1) T = c_p \frac{\kappa - 1}{\kappa} T. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

Now we may also develop different formulas for the entropy  $P$  of gases. If in the last of equations (IIIa), p. 62, we replace the function  $S$  by the absolute temperature  $T$ , we shall also have

$$dQ = A T dP. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53f)$$

If according to equation (54) we express  $B T$  by  $p v$ , we get by substitution in equation (53c)

$$dP = \frac{dQ}{A T} = \frac{c_v}{A} \left( \frac{dp}{p} + \kappa \frac{dv}{v} \right),$$

and there follows, if we divide equations (53d) and (53e) by  $A T$ ,

$$dP = \frac{c_v}{A} \left( \frac{dT}{T} + (\kappa - 1) \frac{dv}{v} \right)$$

and

$$dP = \frac{c_p}{A} \left( \frac{dT}{T} - \frac{\kappa - 1}{\kappa} \frac{dp}{p} \right).$$

If we integrate these equations and respectively represent the integration constant by  $P_0$ ,  $P_0'$ , and  $P_0''$ , which to be sure in most cases of application disappears from the formulas, we get

$$P = P_0 + \frac{c_v}{A} \log_e (pv^\kappa), \quad . \quad . \quad . \quad . \quad . \quad (55a)$$

or

$$= P_0' + \frac{c_p}{A} \log_e (Tv^{\kappa-1}), \quad . \quad . \quad . \quad . \quad . \quad (55b)$$

or finally

$$= P_0'' + \frac{c_p}{A} \log_e \left( \frac{T}{p^{\frac{\kappa-1}{\kappa}}} \right). \quad . \quad . \quad . \quad . \quad . \quad (55c)$$

All the equations just developed are true for the unit of weight (1 kg.) [1 lb.] of gas; consequently if for such a unit there are given two of the three quantities  $p$ ,  $v$ , and  $T$ , we can determine the third from equation (54) and can then determine easily the entropy  $P$  from one of the equations 55; on the other hand, the utilization of equation (53), for the determination of the quantity of heat  $Q$  for any finite change of state of the gas, demands a statement of the way in which the change has taken place. It will be the task of the following investigations to carry through the calculations for a series of the most important of these changes.

But equation (53b) calls for a particular remark; if we replace in it, in accordance with the ordinary usage, the absolute temperature  $T$  by the temperature  $t$ , we get

$$dQ = c_v dt + A p dv.$$

The heat to be imparted to the gas accordingly divides itself into two parts, of which the part  $c_v dt$  consumed in the gas just corresponds to the quantity of heat which must be supplied to the gas if it is to experience this rise of temperature a t c o n s t a n t

v o l u m e; therefore this part consumed in the interior of the gas must always be the same, whatever change the gas may experience in the way of pressure and volume. The truth of this is so evident that we might have written the preceding equation at once; the combination of the equation with the equation of condition of gases (the law of M a r i o t t e and G a y - L u s s a c) then easily and directly leads to the equations found above for gases.

## § 26. THE ISOTHERMAL AND ISODYNAMIC CURVE FOR GASES.

The “ i s o t h e r m a l c u r v e ” (§ 6, p. 39) gives the law according to which a body experiences reversible changes of state, during heat supply or heat withdrawal, while the temperature  $T$  is kept constant and the pressure  $p$  varies with the volume  $v$ .

We get especially and immediately for gases from the equation of condition

$$pv = BT,$$

and for the equation of the curve sought

$$pv = p_1v_1,$$

when the initial condition is given by the quantities  $p_1$ ,  $v_1$ , and  $T_1$  because  $T = T_1$ .

The isothermal curve for gases is therefore an “equilateral hyperbola” whose constant  $p_1v_1 = BT_1$  is determined by the initial condition, and indeed, if we here assume a unit of weight of a gas, it is completely determined by the initial temperature  $T_1$  alone.

The “ i s o d y n a m i c c u r v e ” represents (§ 6, p. 37) the change of the pressure  $p$  with the volume  $v$ , when the energy or inner work  $U$  is kept constant during the change of state; the heat imparted or withdrawn is therefore completely transformed into outer work or generated by such work, respectively. But from equations (52) and (52*b*), p. 132, and an assumption of a constant value of  $U$ , we see that then the product  $pv$  and the

temperature  $T$  are each constant. In gases, therefore, the isodynamic curve is identical with the isothermal curve.

If we expand the unit of weight of gas isothermally or isodynamically from the volume  $v_1$  to the volume  $v$  (Fig. 19a), we can easily draw the transformation  $a'b'$  of the pressure curve  $ab$ , provided in Fig. 19b we lay off corresponding heat weights as abscissas and the temperatures  $T_1$  as ordinates. We

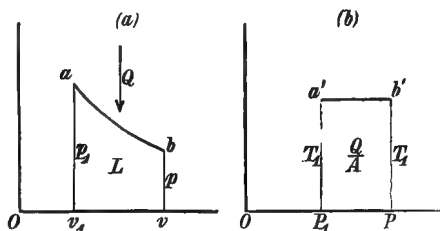


FIG. 19.

compute according to equation (55a) the value  $P_1$  for the initial condition  $(p_1, v_1)$  and the value  $P$  for the final condition  $(p, v)$ ; these in Fig. 19b make

$$OP_1 = \frac{c_v}{A} \log_e p_1 v_1^{\kappa} \quad \text{and} \quad OP = \frac{c_v}{A} \log_e p v^{\kappa},$$

and draw the horizontal  $a'b'$  corresponding to the ordinate  $T_1$ .

The area bounded by the pressure curve  $ab$  represents the work performed during expansion, while the area  $P_1a'b'P$  given in the transformation represents the quantity of heat  $Q$ , measured in units of work, which was supplied to the gas from the outside during the assumed change of state.

The quantity of heat can be computed from equations (53d) and (53e), because  $T = T_1$  and  $dT = 0$ , by the integration

$$Q = c_v(\kappa - 1)T_1 \log_e \frac{v}{v_1} = c_p \frac{\kappa - 1}{\kappa} T_1 \log_e \frac{p_1}{p}, \quad . \quad . \quad (56a)$$

or, considering the relations given in equation (54), it can be found from

$$Q = ABT_1 \log_e \frac{v}{v_1} = ABT_1 \log_e \frac{p_1}{p}, \quad . \quad . \quad . \quad (56b)$$

and considering the equation of condition:

$$= Ap_1 v_1 \log_e \frac{v}{v_1} = Ap_1 v_1 \log_e \frac{p_1}{p}. \quad . \quad . \quad . \quad (56c)$$



Because, for an invariable value of  $U$ , the heat  $Q$  is supplied completely transformed into work, we have

$$Q = AL, \quad . . . . . (57)$$

and therefore we find the work performed or consumed during isothermal or isodynamic expansion or compression from the equations (56*b*) or (56*c*) is

$$L = BT_1 \log_e \frac{v}{v_1} = BT_1 \log_e \frac{p_1}{p}, \quad . . . . (58a)$$

or

$$L = p_1 v_1 \log_e \frac{v}{v_1} = p_1 v_1 \log_e \frac{p_1}{p}. \quad . . . . (58b)$$

From equation (57) it is evident that the transformation  $a'b'$  of the pressure curve here considered (Fig. 19) covers the same area  $L$  as the pressure curve itself, a proposition which is more-over true for the isothermal curve of every body.

**Example.**—Let us suppose one kilogram [one pound] of atmospheric air of the temperature  $t_1 = 15^\circ \text{C}$ . [ $59^\circ \text{F}$ .] to expand isothermally from the initial pressure 2.5 atmospheres to 1 atmosphere, then  $p_1 = 2.5 \times 10333$  and  $p = 1 \times 10333$  [ $p_1 = 36.742$  and  $p = 14.6967$  lb. per sq. in.] and  $T_1 = 288^\circ \text{C}$ . [ $T_1 = 518.4^\circ \text{F}$ .]; consequently it follows from the equation of condition because  $B = 29.269$  [ $B = 53.349$ ] for air, that the specific volume at the beginning and at the end is  $v_1 = 0.3263$  cbm. [5.227 cu. ft.] and  $v = 2.5v_1 = 0.8158$  cbm. [13.068 cu. ft.], and therefore according to equation (58) the work performed is  $L = 7723.85$  mkg. [25340.78 ft-lb.], and the quantity of heat imparted to maintain the temperature constant:  $Q = AL = 18.217$  cal. [32.79 B.t.u.].

According to equation (55*a*) there results for the entropy of air at the beginning and at the end:

$$\begin{aligned} P_1 &= 371.78 \quad \text{and} \quad P = 398.60 \\ [P_1 &= 902.27 \quad \text{and} \quad P = 951.21], \end{aligned}$$

because the specific heat  $c_v = 0.1685$  and  $\kappa = 1.410$ ; consequently we can find the work from the expression  $L = (P - P_1)T_1$ .

The formulas (58*b*) given above for the external work  $L$  have long been extensively used in Physics and Mechanics and in the Theory of Engines, long before the rise of the Thermodynamics of the present day. The assumption that the expansion and com-

pression took place according to the equilateral hyperbola was a natural one; but that such a change of state of the gas could only result from a suitable supply or withdrawal of heat was first made clear by investigations based on the laws of Thermodynamics; that is why this sort of change of state was assumed in cases in which it is not at all permissible, for example in the efflux problem; it is remarkable that this occurs even now, and is an assumption which may still be found in some of the elementary manuals of Physics and of Mechanics.

## § 27. THE ADIABATIC CURVE OF GASES.

If, during a reversible change of state of a gas, heat is neither imparted nor withdrawn either during the whole course or in any of its parts, then the pressure  $p$  of a gas will change with its volume according to a curve designated as the “*a d i a b a t i c c u r v e*” (see § 6, p. 39).

During the adiabatic change of state the temperature  $T$  also simultaneously changes with the pressure and volume according to a particular law; the changes in question follow directly from equations (55a) to (55c), p. 135, given for the entropy  $P$  of gases.

Because  $dQ=0$ , for all elements of the change of state under the assumption made, there follows, from equation (53f),  $dP=0$ ; consequently the entropy  $P$  is equally large for all points of the adiabatic; therefore from equation (55a) we have for the initial and final condition (Fig. 20)

$$P = \frac{c_v}{A} \log_e p_1 v_1^\kappa = \frac{c_v}{A} \log_e p v^\kappa, \quad . \quad . \quad . \quad . \quad (59)$$

provided we make the arbitrary constant  $P_0$  equal to zero; hence the equation of the adiabatic curve can also be represented simply by

$$p v^\kappa = p_1 v_1^\kappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

In the same way there can be determined from equations (55b) and (55c)

$$\frac{T}{T_1} = \left( \frac{v_1}{v} \right)^{\kappa-1} \quad \text{and} \quad \frac{T}{T_1} = \left( \frac{p}{p_1} \right)^{\frac{\kappa-1}{\kappa}}, \quad . \quad . \quad . \quad (61)$$

from which we can find the temperature  $T$  for any point of the adiabetic corresponding to a given value of  $v$  or  $p$ .

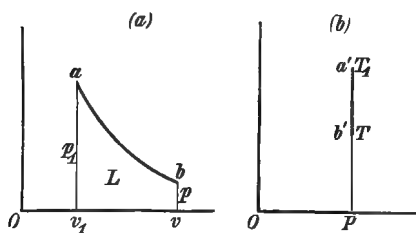


FIG. 20.

The transformation of the adiabetic curve  $ab$  (Fig. 20a) is given by the straight line  $a'b'$  (Fig. 20b).

The foregoing results (60) and (61) would also have been given by equations (53c) to (53e), if we had there made  $dQ=0$  and integrated.

The work  $L$ , which is performed or consumed during adiabetic expansion or compression respectively, can be computed from equation (53b), p. 134, when we put  $dQ=0$ , and integrate the equation:

$$Apdv = -c_v dT,$$

from which follows

$$L = \frac{c_v}{A}(T_1 - T). \quad . \quad . \quad . \quad . \quad . \quad . \quad (62a)$$

If we use the relation (54) here, we can also write

$$L = \frac{1}{\kappa - 1}(p_1 v_1 - pv), \quad . \quad . \quad . \quad . \quad . \quad (62b)$$

or by using formulas (61)

$$L = \frac{c_v T_1}{A} \left[ 1 - \left( \frac{v_1}{v} \right)^{\kappa-1} \right] = \frac{c_v T_1}{A} \left[ 1 - \left( \frac{p}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right]. \quad . \quad (63)$$

In these two equations we can also replace the factor in front of the parenthesis by

$$\frac{c_v T_1}{A} = \frac{p_1 v_1}{\kappa - 1}.$$

Moreover equation (62b) shows that for any adiabetic change of state the work is proportional to the difference of the two rectangles  $p_1 v_1$  and  $pv$  constructed from the initial and final coordinates.



its influence is the more subordinate, the more the vapor approaches to the condition of a gas; if the latter obeys the law of *M a r i o t t e* and *G a y - L u s s a c*, as was assumed in the above investigations, then we must substitute  $R=0$ .

If we regard  $R$  as a function of  $p$  and  $v$ , and if we differentiate equation (64) partially with respect to  $p$  and  $v$ , and use for the absolute temperature the relation  $T=a+t=273+t[459.4+t]$ , we get

$$B \frac{\partial t}{\partial v} = p + \frac{\partial R}{\partial v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

$$B \frac{\partial t}{\partial p} = v + \frac{\partial R}{\partial p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

Let us first compute the coefficients of expansion  $\alpha_v$  and  $\alpha_p$ , which were already discussed on p. 97. We found for their reciprocal values  $a_v$  and  $a_p$ , from equation (6) there given,

$$a_v = p \frac{\partial t}{\partial p} - t \quad \text{and} \quad a_p = v \frac{\partial t}{\partial v} - t,$$

and therefore there result for  $T=a+t$ , and the preceding formulas (64), (65), and (66),

$$B(a - a_v) = R - p \frac{\partial R}{\partial p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

$$B(a - a_p) = R - v \frac{\partial R}{\partial v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

According to these equations the two values  $a_v$  and  $a_p$  and the two coefficients of expansion  $\alpha_v$  and  $\alpha_p$  could be computed for the body in question if the function  $R$  in the equation of condition (64) were known.

Now if heat supply under constant volume or constant pressure takes place, we have  $dv=0$  or  $dp=0$  respectively; from the second and third of equations (36), p. 122, there follows

$$dQ_v = \frac{A X}{\frac{\partial t}{\partial p}} dt, \quad dQ_p = \frac{A Y}{\frac{\partial t}{\partial v}} dt.$$

Let  $c_v$  and  $c_p$  be the specific heats of the body at constant volume and at constant pressure respectively, then

$$dQ_v = c_v dt \quad \text{and} \quad dQ_p = c_p dt,$$

and by combining with the preceding expression there follows

$$AX = c_v \frac{\partial t}{\partial p} \quad \text{and} \quad AY = c_p \frac{\partial t}{\partial v}.$$

If we utilize these values in equations (Ia), (IIa), and (IIIa), p. 62, the first fundamental equation takes the form

$$\frac{\partial}{\partial p} \left( c_p \frac{\partial t}{\partial v} \right) - \frac{\partial}{\partial v} \left( c_v \frac{\partial t}{\partial p} \right) = A, \quad . . . . \quad (\text{Ib})$$

and the second fundamental equation

$$(c_p - c_v) \frac{\partial t}{\partial v} \frac{\partial t}{\partial p} = AT, \quad . . . . \quad (\text{IIb})$$

and there further follow

$$\left. \begin{aligned} dQ &= c_v \frac{\partial t}{\partial p} dp + c_p \frac{\partial t}{\partial v} dv \\ &= c_v dt + \frac{AT}{\frac{\partial t}{\partial p}} dv \\ &= c_p dt - \frac{AT}{\frac{\partial t}{\partial v}} dp \end{aligned} \right\} . . . . \quad (\text{IIIb})$$

From equation

$$dQ = AdU + Apdv$$

we can then compute the change of energy  $dU$ ; for example, there follows from the second of equations (IIIb)

$$AdU = c_v dt + A \left( \frac{T}{\frac{\partial t}{\partial p}} - p \right) dv. \quad . . . . \quad (\text{IVb})$$

We will repeatedly emphasize the fact that these equations are perfectly valid and general for the equation of condition (64), that is, for  $pv + R = BT$ , the specific heats  $c_p$  and  $c_v$  being here regarded as functions of  $p$  and  $v$ .

The formulas permit a number of transformations if we employ, for the partial differential coefficients  $\frac{\partial t}{\partial v}$  and  $\frac{\partial t}{\partial p}$ , equations (65) and (66), and as occasion may demand also utilize equations (67) and (68), in which  $a_v$  and  $a_p$  are taken as functions of  $p$  and  $v$ ; for example, we see that in place of equation (IVb) we can put

$$AdU = c_v dt + \frac{Ap(a - a_v)}{a_v + t} dv.$$

The formulas become immediately available if we only know the law of change of two of the quantities  $R$ ,  $c_p$ , and  $c_v$ , regarded as functions of  $p$  and  $v$ . In subsequent investigations of vapors the different assumptions which have hitherto been made concerning the function  $R$  will be more fully discussed; at this place only one case will be subjected to special consideration; it will be assumed that we have before us a gas obeying the law of Mariotte and Gay-Lussac. Assume, therefore, the equation of condition, as in former investigations, to be  $pv = BT$ , consequently  $R = 0$ .

Here equations (67) and (68) give at once

$$a_v = a_p = a = 273 [491.4],$$

and from equations (65) and (66) follow

$$B \frac{\partial t}{\partial v} = p \quad \text{and} \quad B \frac{\partial t}{\partial p} = v.$$

Substitution in equation (IIb) then gives

$$c_p - c_v = AB, \quad . \quad . \quad . \quad . \quad . \quad . \quad (68a)$$

and after a few simple transformations there follows from equation (Ib)

$$p \frac{\partial c_p}{\partial p} = v \frac{\partial c_v}{\partial v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

The next to the last equation shows that the difference of the specific heats is constant even if they do vary with  $p$  and  $v$ ; if we differentiate the equation with respect to  $v$  and substitute  $\frac{\partial c_p}{\partial v} = \frac{\partial c_v}{\partial v}$  in the last equation, there follows the relation

$$p \frac{\partial c_p}{\partial p} = v \frac{\partial c_p}{\partial v},$$

which differential equation is only satisfied when  $c_p$  is regarded as a function of the product  $pv$ ; but as this product is proportional to the absolute temperature  $T$ , there follows for  $R=0$ ,

(1) That the specific heat  $c_p$  for constant pressure, if it is variable at all, can only be a function of the temperature  $t$ , and

(2) That the specific heat  $c_v$  for constant volume, according to equation (68a), can differ from the value of  $c_p$  only by a constant.

There exist valuable experiments by Eilhard Wiedemann<sup>1</sup> on the variability of the specific heat  $c_p$  with the temperature. He found for atmospheric air  $c_p=0.2389$ , for hydrogen  $c_p=3.4100$ , for carbonic oxide  $c_p=0.2425$ , values which differ very little from the results of Regnault. It was also found by E. Wiedemann that these values (within the ordinary pressure and temperature limits) were independent of the temperature. On the other hand he found an increase of the values  $c_p$  with the temperature, for the following gases:

for $t=$	0°	100°	200° C.
	[32°]	[212°]	[392° F.]
Carbonic acid, $c_p=$	0.1952	0.2169	0.2387
Ammonia.....	0.5009	0.5317	0.5629
Ethylene.....	0.3364	0.4189	0.5015
Nitric oxide.....	0.1983	0.2212	0.2442

For that matter Regnault has already shown that for carbonic acid in particular there was an increase of specific heat with the temperature; he<sup>2</sup> found for 0°, 100°, and 200° [32°, 212°, 392° F.]

<sup>1</sup> E. Wiedemann, "Über die spezifische Wärme der Gase." Poggen-dorff's Annalen, vol. 157, p. 1.

<sup>2</sup> Rel. II, 130.



392° F.], respectively,  $c_p = 0.1870, 0.2145$ , and  $0.2396$ , values which differ little from those found by E. Wiedemann..

Later the question was again examined by Mallard and Le Chatelier,<sup>1</sup> and their work has created great interest among the engineers of Germany, because they touched questions which play an important part in judging gas- (explosive) engines and in the investigation of combustion phenomena in general; the problem here is mainly the behavior of the products of combustion of exploding gases, namely, of carbonic acid and of vapor of water.

Let  $m$ , as above, be the molecular weight of the gas or vapor, as the case may be, then we can write

$$mc_v = \alpha + \beta t + \gamma t^2, \dots \dots \dots (70)$$

when  $c_v$  represents the specific heat at constant volume and  $\alpha$ ,  $\beta$ , and  $\gamma$  are experimental constants. Consequently the heat  $Q$  necessary for heating from  $0^\circ$  to  $t^\circ$  is

$$Q = \int_0^t mc_v dt = \alpha t + \frac{\beta t^2}{2} + \frac{\gamma t^3}{3}.$$

The equation can also be written

$$Q = [\alpha + \frac{1}{2}\beta t + \frac{1}{3}\gamma t^2]t,$$

where we can consider the quantity enclosed in the bracket as the mean specific heat  $c_m$  between the temperatures  $0^\circ$  and  $t^\circ$ ; consequently we can write

$$\begin{aligned} c_m &= \alpha + \frac{1}{2}\beta t + \frac{1}{3}\gamma t^2 \\ &= \alpha + \beta' t + \gamma' t^2. \end{aligned}$$

Accordingly we should get for equation (70)

$$\beta = 2\beta' \quad \text{and} \quad \gamma = 3\gamma',$$

provided  $\beta'$  and  $\gamma'$  were known from experiments.

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<sup>1</sup> "Recherches expérimentales et théoriques sur la combustion des mélanges gazeux explosifs," by Mallard and Le Chatelier, Ingénieurs au corps de Mines. Annales des Mines, Vol. IV, 1883.

Mallard and Le Chatelier have recomputed their original observations, making use of the experimental results of Sarrau and Vieille, and got for the mean specific heat  $c_m$  the following expressions:<sup>1</sup>

$$\left. \begin{array}{ll} \text{for carbonic acid.} & c_m = 6.50 + 0.00387 t, \\ \text{" steam} & = 5.78 + 0.00286 t, \\ \text{" the simple gases (H}_2\text{, O}_2\text{, N}_2\text{, CO)} & = 4.76 + 0.00122 t. \end{array} \right\} . \quad (\alpha)$$

From this follows, for molecular weight, the specific heat at constant volume:

$$\left. \begin{array}{ll} \text{for carbonic acid} & mc_v = 6.50 + 0.00774 t, \\ \text{" steam} & = 5.78 + 0.00572 t, \\ \text{" the simple gases} & = 4.76 + 0.00244 t. \end{array} \right\} . \quad (\beta)$$

If we introduce the absolute temperature, putting  $t = T - 273$  we get:

$$\left. \begin{array}{ll} \text{for carbonic acid} & mc_v = 4.387 + 0.00774 T, \\ \text{" steam} & = 4.218 + 0.00572 T, \\ \text{" the simple gases.} & = 4.094 + 0.00244 T. \end{array} \right\} . \quad (\gamma)$$

It follows from this, as is also pointed out by Le Chatelier, that at the absolute zero the real specific molecular heats would be nearly equal for the gases and vapors before us.

As the relation  $mc_p - mc_v = 1.9934$ , equation (46), p. 126, holds, we can compute the specific heat  $c_p$  at constant pressure from the foregoing formulas, but of course the values for carbonic acid and the vapor of water must be regarded as approximations only.

If we substitute in the second group of the preceding expressions  $m = 44$ , we get for carbonic acid

$$\begin{aligned} c_v &= 0.1477 + 0.000176 t, \\ c_p &= 0.1930 + 0.000176 t; \end{aligned}$$

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<sup>1</sup> Wiedemann's Beiblätter zu den Annalen der Physik und Chemie, 1890, XIV, p. 365.

for the vapor of water with  $m=18$ :

$$\begin{aligned}c_v &= 0.3211 + 0.000318 \, t, \\c_p &= 0.4318 + 0.000318 \, t;\end{aligned}$$

for hydrogen, because  $m=2$ :

$$\begin{aligned}c_v &= 2.380 + 0.00122 \, t \\c_p &= 3.377 + 0.00122 \, t.\end{aligned}$$

For other gases, oxygen, nitrogen, and carbonic oxide we would put respectively  $m=32$ , 28, and 28. These formulas give for carbonic acid and the vapor of water, values for  $c_p$  between the temperatures  $0^\circ$  and  $200^\circ$  [ $32^\circ$  and  $392^\circ$  F.], which agree sufficiently well with the formerly given values of Regnault and E. Wiedemann; for hydrogen and the other simple gases the specific heats experience such a marked increase with the temperature that the author felt justified, when issuing the preceding edition of this book, in doubting the reliability of the experimental results of Mallard and Le Chatelier.

In the meantime these investigations have been confirmed in a general way by the new experiments of A. Langen<sup>1</sup> and have been utilized in the more recent technical investigations on internal-combustion motors by Stodola, E. Meyer, and others, so that we may consider the doubt raised as removed although the problem cannot be regarded as solved in all its parts. At any rate there must be dropped from the theory of internal-combustion motors the former assumption of the constancy of the specific heats of the products of combustion, although we may still be far from a satisfactory theory of the occurrences in said engines. That the specific heats can be assumed to vary only with the temperature, in gases subject to the equation of condition  $pv=BT$ , was discussed upon p. 145, but it is just the products of combustion, carbonic acid and steam, upon which everything here depends, that do not obey this law; here the specific heats must be regarded as also depending on the pressure. Considering this de-

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<sup>1</sup> A. Langen, Untersuchungen über die Drucke, welche bei Explosionen von Wasserstoff und Kohlenoxyd in geschlossenen Gefässen auftreten. (Zeitschrift des Vereins deutscher Ingenieure, 1903, p. 622.)

pendence on temperature and pressure at their higher values, there is at present complete uncertainty.

To this must be added the circumstance that at high temperatures carbonic acid and steam experience "Dissociation," a decomposition into their constituents, a procedure concerning whose laws there likewise exists complete uncertainty.

In the observations of *Langen*, as well as in those of *Mallard* and *Le Chatelier*, connected with the cooling curves of those experiments relating to temperatures above  $1700^{\circ}\text{C}$ . [ $3100^{\circ}\text{F}$ .] after the combustion of carbonic acid, there occurred irregularities which can only be explained by the dissociation of carbonic acid.

Therefore for combustion temperatures above  $1700^{\circ}\text{C}$ . [ $3100^{\circ}\text{F}$ .] the above-given formulas for molecular heats cannot be employed.

For gases (atmospheric air) there is on hand a special investigation by *Linde*.<sup>1</sup> In a clever way *Linde* based and built his machine for the liquefaction of atmospheric air upon certain occurrences in an experimental series by *W. Thomson* and *Joule*, which have been known since 1862, and which previously had only occasionally given rise to theoretical considerations concerning the behavior of gases. On the basis of these experiments and by considering certain occurrences in his machine *Linde* (*ibid.*) obtained the following formula for the computation of the specific heats  $c_p$  of the air at constant pressure. Into the development of this formula we will go more fully later on, in the theory of vapors and when considering *Linde's* machine. But at this place we must emphasize what is of importance for the following investigations of air and gas engines. *Linde's* formula reads:

$$c_p = c_{p_0} \left[ 1 - \frac{3\alpha p}{T^3} \right]^{-\frac{2}{3}}.$$

Here  $c_{p_0} = 0.237$ , which value, according to *Witkowski's* experimental results, represents the specific heat  $c_p$  at very

<sup>1</sup> *Linde*, "Über die Veränderlichkeit der spezifischen Wärme der Gase." Sitzungsberichte der mathem.-physik. Klasse der k. bayer. Akademie der Wissenschaften, Vol. XXVII, 1897, No. 3.

small values of the pressure  $p$  lying near to zero, and is independent of the temperature. We must write for the constant  $\alpha$  when  $p$  is expressed in atmospheres (10333 kg. per qm.) [14.6967 lb. per sq. in.],  $\alpha = 20570$  [ $\alpha = 8163$  for  $p$  in lb. per sq. in. and  $T$  in Fahr. degrees].

The following table is computed by the preceding equation and gives in somewhat more extended form Linde's table (ibid.) for the specific heat  $c_p$  of air.

	$t = -100^\circ$ $t = [-148^\circ]$	$-50^\circ$ $[-58^\circ]$	$0^\circ$ $[32^\circ]$	$+100^\circ \text{ C.}$ $[+212^\circ \text{ F.}]$
$p = 1 \text{ Atm.}$	0.2389	0.2379	0.2375	0.2372
10 "	0.2579	0.2462	0.2419	0.2389
40 "	0.3650	0.2801	0.2583	0.2448
70 "	0.7856	0.3293	0.2779	0.2511

At the same temperature the values of  $c_p$  show an increase with the pressure, and this is more marked the lower the temperature, that is, the nearer the air is to liquefaction. And for the same pressure the values diminish continuously with increasing temperature, and for all pressures would approach to the constant value 0.2370; the latter result contradicts the above-mentioned observations of Mallard and Le Chatelier and also those of Langen, but of course it must here be remembered that Linde's formula for  $c_p$  is only to be regarded as decisive within narrow limits.

In any case we can draw the conclusion that for temperatures from  $-50^\circ$  to  $+100^\circ$  [ $-58^\circ$  to  $+212^\circ$ ] and over, and for pressures deviating but little from one atmosphere, Regnault's constant average value 0.2375 is thoroughly reliable, so that in the theory of hot- and cold-air engines air can be assumed as a perfect gas.

# APPLICATIONS.

## PHYSICAL PART.

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### I. Reversible Changes of State of a Gas.

#### § 29. THE POLYTROPIC CURVE OF GASES.

Of the numerous pressure curves, which a gas may follow when experiencing reversible changes of state, there is one case of special importance, because it includes numberless special cases and just the ones which are of physical and of technical importance. The problem indicated embraces the behavior of the gas under the assumption that "the quantity of heat supplied to, or withdrawn from, the gas is directly proportional to the change of temperature."

Suppose given the unit of weight of a gas, the pressure  $p$ , volume  $v$ , and temperature  $T$ ; the pressure curve is to be determined when the quantity of heat for an infinitesimal change of state is given by

$$dQ = cdT, \quad . . . . . (1)$$

in which  $c$  represents any positive or negative, whole or fractional, number. According to equation (54), p. 134, the equation of condition is written in the form

$$Apv = c_v(\kappa - 1)T.$$

If we differentiate it and substitute the value of  $dT$  in the foregoing equation (1), there follows, for the case assumed,

$$dQ = \frac{A}{\kappa - 1} \frac{c}{c_v} (vd p + p dv).$$

On the other hand we have generally, for every kind of change of state, according to equation (53c), p. 134,

$$dQ = \frac{A}{\kappa - 1} (vdp + \kappa pdv).$$

By equating these two expressions and remembering that  $c_p = \kappa c_v$ , we get

$$(c - c_v)vdp + (c - c_p)pdv = 0.$$

If we divide both sides by  $(c - c_v)pv$  and put

$$\frac{c - c_p}{c - c_v} = n, \quad . . . . . (2)$$

where  $n$  is a new constant quantity, completely determined by the value of  $c$ , by the specific heat for constant pressure ( $c_p$ ), and by that for constant volume ( $c_v$ ), we get

$$\frac{dp}{p} + n \frac{dv}{v} = 0,$$

and from this, by integration,

$$pv^n = C, \quad . . . . . (3)$$

where  $C$  represents a constant.

If the initial condition is given by  $p_1$  and  $v_1$ , we accordingly have

$$pv^n = p_1 v_1^n \quad . . . . . (3a)$$

as the equation of the sought pressure curve, which we will hereafter call the *polytropic curve*. If at the start there is given, instead of the factor  $c$ , the exponent  $n$  of the preceding formula, then we can compute backward from equation (2) and get

$$c = \frac{n - \kappa}{n - 1} c_v. \quad . . . . . (4)$$

I call  $c$  the "specific heat of the gas for the pressure curve  $pv^n = C$ ." <sup>1</sup>

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<sup>1</sup> I first called attention to this general case of the change of condition of a gas in the second edition of this book (1866). Since that time the corresponding formulas and propositions have been much used, particularly in technical investigations.

Because of the arbitrary choice of the exponent  $n$  there are therefore an infinite number of values of the specific heat; but only on the assumption of this kind of pressure curve is the quantity of heat proportional to the change of temperature.

If we write the equation of condition in the form

$$\frac{pv}{p_1v_1} = \frac{T}{T_1},$$

its combination with equation (3) also gives

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{n-1} \quad \text{and} \quad \frac{T}{T_1} = \left(\frac{p}{p_1}\right)^{\frac{n-1}{n}}, \dots \dots (5)$$

from which equations can be directly determined the temperature  $T$  for every pressure-curve point which is fixed by a corresponding value of the volume  $v$  or of the pressure  $p$ .

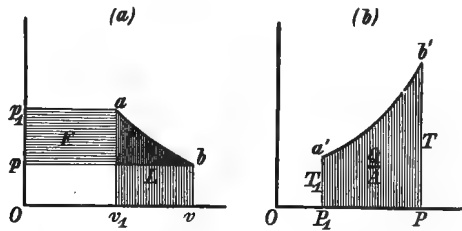


FIG. 21.

The quantity of heat which must be supplied for the change corresponding to the pressure curve  $ab$  (Fig. 21) can be found at once, from equation (1), to be

$$Q = c(T - T_1), \dots \dots \dots (6)$$

and the work performed is determined by the integration of equation (53b), p. 134:

$$L = \frac{(c - c_v)}{A}(T - T_1). \dots \dots \dots (7)$$

Dividing this formula by equation (6) gives

$$\frac{AL}{Q} = \frac{c - c_v}{c}, \dots \dots \dots (7a)$$



according to which the external work is likewise proportional to the change of temperature, and therefore also directly proportional to the quantity of heat  $Q$ .

If in equation (7) we replace the specific heat  $c$  by the value given in equation (4), we get, by considering equation (54), p. 134,

$$c - c_v = -\frac{c_v(\kappa - 1)}{n - 1} = -\frac{AB}{n - 1},$$

and from this also the external work:

$$L = \frac{1}{n - 1}(p_1 v_1 - pv), \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

or

$$L = \frac{p_1 v_1}{n - 1} \left[ 1 - \left( \frac{v_1}{v} \right)^{n-1} \right] = \frac{p_1 v_1}{n - 1} \left[ 1 - \left( \frac{p}{p_1} \right)^{\frac{n-1}{n}} \right], \quad . \quad . \quad (7c)$$

in which latter formulas the factor  $p_1 v_1$  can be replaced by  $BT_1$ .

Equation (7b) seems to be particularly simple. The external work  $L$ , represented in Fig. 21a by the vertically hatched area, appears as proportional to the difference of the two rectangles formed by the pressure and volume at the beginning and at the end of the operation.

If we determine in Fig. 21a by the planimeter the area  $L$  and the two rectangles, we can find from equation (7b) the exponent  $n$  and then also the specific heat  $c$ , provided of course that the pressure curve is really subject to the law  $pv^n = \text{constant}$ .

In certain investigations into which we will enter later, the area  $p_1 abp$ , bounded by the pressure curve  $ab$  and distinguished in Fig. 21a by partially horizontal and partially close hatchings, plays an important part. If we designate this area by  $F$  we get, as the figure shows,

$$F = p_1 v_1 + L - pv,$$

and therefore with the help of equation (7b)

$$F = \frac{n}{n - 1}(p_1 v_1 - pv), \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and by the combination of the two equations we get

$$\frac{F}{L} = n, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

which formula will still more easily lead to the exponent  $n$ , with the help of the planimeter.

The use of equation (6) in equation (7b) leads to the formula

$$Q = \frac{\kappa - n}{\kappa - 1} AL, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

or with the help of (9) to

$$Q = \frac{A}{\kappa - 1} (\kappa L - F), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10a)$$

and with this and the planimeter we can directly determine the quantity of heat  $Q$  which can be imparted during the change of condition given by the drawing.

The foregoing can even then be applied when the law of the change of state is not known, and when this change is not subject to the condition  $pv^n = \text{constant}$ .

For if we suppose the pressure curve  $ab$  (Fig. 21a) to represent a part of the curve of an indicator diagram from a hot- or cold-air engine, and that part which corresponds to the expansion or compression of the air in the engine cylinder, then the curve can be conceived as decomposed into short pieces which approximately follow the foregoing law of change; as we do not here have to do with the unit of weight, let  $V_1$  and  $V_2$  represent the volume at the beginning and the end, and  $p_1$  and  $p_2$  the corresponding pressure for any short piece of curve, both co-ordinates being determined by measurement from the indicator diagram. Then we can put  $p_2 V_2^n = p_1 V_1^n$  and from this derive

$$n = \frac{\log p_1 - \log p_2}{\log V_2 - \log V_1},$$

and then compute from equation (4) the specific heat  $c$ . If we perform this computation for the various parts of the curve, we get an insight as to whether, during the whole expansion or com-

pression, there has been a supply or withdrawal of heat and to what extent it has taken place; in general, different values will be obtained for  $n$  and  $c$  for the separate curve-intervals. This method of investigating the pressure curve has often been practically carried out, but the solution with the help of the "transformation" of the pressure curve furnishes a still better insight into the problem.

### § 30. OTHER PROPERTIES OF THE POLYTROPIC CURVE.

If we suppose different values given to the constant  $C$  of equation (3), p. 152, we will get an infinite multitude of pressure curves having the same law (Fig. 22). The differentiation of the equation gives

$$npdv + vdp = 0,$$

or

$$-\frac{dp}{dv} = n \frac{p}{v}. \quad . \quad . \quad . \quad (11)$$

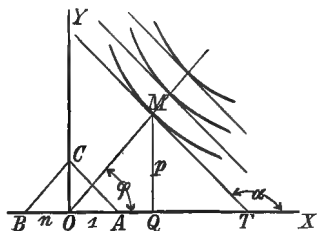


FIG. 22.

Now if  $MTX$  is the angle  $\alpha$  made by the tangent, and  $MOX = \phi$  the angle formed by the radius vector  $OM$  with the axis  $OX$ , then there follows from equation (11)

$$-\tan \alpha = n \tan \phi. \quad . \quad . \quad . \quad . \quad . \quad (11a)$$

consequently the radius vector cuts the whole series of curves at the same angle, that is, the tangents at all these intersections are parallel.

But we also get from the figure

$$\tan \alpha = \frac{MQ}{QT} \quad \text{and} \quad \tan \phi = \frac{MQ}{OQ}.$$

Utilizing these equations in equation (11a) we get simply

$$n = \frac{OQ}{QT}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which shows the exponent  $n$  as the quotient of the abscissa  $OQ$  and the subtangent  $QT$ .

If we lay off from  $O$  on the axis of  $X$  the distance  $OA$  as the unit of length, and if we draw through the point  $A$  the line  $AC$  parallel to the tangent and through the point of intersection  $C$  the line  $CB$  parallel to the radius-vector, then the intercept  $OB$  will give directly the value of the exponent  $n$ , and this gives us an additional means of examining whether or no an assumed pressure curve obeys the law  $pv^n = \text{constant}$ , and if it does not, of ascertaining how  $n$  varies from element to element. Figs. 23a and 23b

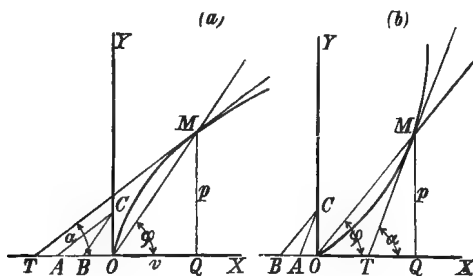


FIG. 23.

give the course of the assumed pressure curve under the assumption that the exponent  $n$  is *negative*.

Fig. 23a is true for the assumption  $n < 1$ , and Fig. 23b for  $n > 1$ ; in both cases the curves pass through the origin  $O$  of the coordinate axes (parabolas of higher order).

For  $QT = 0$  there follows, from equation (12),  $n = \infty$ , then the curve is transformed into a straight line parallel to the axis of ordinates  $OY$ .

In this case equation (4) gives the specific heat  $c = c_v$ ; according to equation (6) there follows the supplied heat  $Q = c_v(T - T_1)$ , and according to equation (7) the external work  $L = 0$ ; we here therefore strike a case, long ago treated in Physics, of heating the gas under constant volume.

On the other hand, if the subtangent  $QT = \infty$ , there follows  $n = 0$  from equation (12), and consequently from equation (4)  $c = \kappa c_v = c_p$ ; the supplied heat, according to equation (6), is

$$Q = c_p(T - T_1),$$

and because here  $p=p_1$  according to equation (3), the external work according to equation (7b) becomes

$$L=p_1(v-v_1).$$

Here we have the long-known case of heating the gas under constant pressure.

Furthermore if we substitute  $n=\kappa$  in the given equations of the general case, then  $c=0$ , according to equation (4), and this assumption leads to the adiabatic curve; all the equations then pass into the forms which we find in § 27 for the adiabatic curve.

Finally, if we assume  $n=1$ , equation (5) gives  $T=T_1$ , and hence  $pv=p_1v_1$ , which result corresponds to the isothermal and isodynamic changes of state; equations (7b) and (10) then give the, to be sure, indeterminate expressions

$$L=\frac{0}{0} \quad \text{and} \quad Q=\frac{0}{0},$$

whose values, however, were found earlier by equations (56b) and (58a), pp. 137 and 138.

Consequently the polytropic curve embraces all the special cases treated above.

### § 31. CONSTRUCTION OF THE POLYTROPIC CURVE AND ITS TRANSFORMATION.

If through the point  $M$  (Fig. 24), whose co-ordinates  $OQ$  and  $QM$  are designated by  $v_1$  and  $p_1$ , there is to be passed a polytropic curve, for the law  $pv^n=p_1v_1^n=\text{constant}$ , we can derive a simple method of construction from the following considerations<sup>1</sup>: Draw the line  $OA$ , making any angle  $XOA=\alpha$  with the axis  $OX$ , and likewise draw the line  $OB$ , making the angle  $BOY=\beta$  with the axis  $OY$ ; we now pass vertically downward from the point  $M$  to the intersection  $S$  with the direction  $OA$  and then horizontally over to the intersection  $T$  with the axis  $OY$ ; furthermore, pass

<sup>1</sup> According to Brauer: "Konstruktion gesetzmäßiger Expansionskurven von der allgemeinen Form  $pv^n=C$ ." Zeitschrift des Vereins deutscher Ingenieure, 1885, vol. 29, p. 433.

through the points  $S$  and  $T$  the lines  $SR$  and  $TU$ , making an angle of  $45^\circ$  with the horizontal, and if we draw through  $R$  a vertical, and through  $U$  a horizontal, they will intersect in the point  $N$ , whose co-ordinates  $OR$  and  $RN=OV$  will be designated by  $v$  and  $p$ . According to the given construction  $QS=QR=v-v_1$  and  $VT=UV=p_1-p$ , and consequently

$$\tan \alpha = \frac{v-v_1}{v_1} \quad \text{and} \quad \tan \beta = \frac{p_1-p}{p},$$

or

$$v = v_1(1 + \tan \alpha) \quad \text{and} \quad p_1 = p(1 + \tan \beta).$$

If the point  $N$  is to be a point of the polytropic curve passing through  $M$ , there must hold the relation

$$pv^n = p_1v_1^n,$$

or, utilizing the two preceding expressions, determining from them  $p$  and  $v$  and then substituting, we get the equation

$$(1 + \tan \beta) = (1 + \tan \alpha)^n.$$

If the exponent  $n$  of the polytropic curve is given and the angle  $\alpha$  chosen arbitrarily, we can compute from this equation the angle  $\beta$ , and in Fig. 24 make  $\angle XO A = \alpha$  and  $\angle YOB = \beta$ . Now the rule for construction is simply the following, as may easily be seen. We start down vertically from the given point  $M$  to the point  $S$ , pass horizontally over to the point  $T$  and draw between the lines  $OX$  and  $OA$ , as well as between  $OY$  and  $OB$ , the zigzag lines shown in the figure, in which a part of each broken line is inclined at an angle of  $45^\circ$  to the horizontal. The zigzag may also start from  $S$  and go to the left, and may start from  $T$  and be continued upward. If we now draw vertical lines through all intersections with the axis  $OX$  and horizontal lines through all intersections with the axis  $OY$ , we will get a net of straight lines intersecting

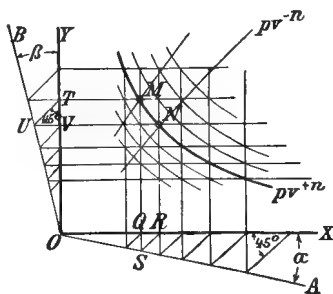


FIG. 24.

each other at right angles, and the corresponding intersections will lie on the curve sought. We see that in this way we not only get the polytropic curve passing through the point  $M$ , but a whole host of curves of the same species. The smaller the angle  $\alpha$  chosen for the construction the nearer to each other will be the sought points of the curves.

Fig. 24 at once gives the course of the curve:

$$pv^{-n} = C.$$

In the net of rectangles we connect in each rectangle the lower left corner with the upper right corner by a straight line, and we get a series of curves corresponding to the preceding equation. All of the curves pass through the origin  $O$  (higher parabolas), but are transformed into straight lines for  $n=1$ , forming a bundle of rays; the corresponding curves, for  $n=+1$ , then form a group of equilateral hyperbolas, for whose construction it is simply necessary to make the angles  $\alpha$  and  $\beta$  equal.

We now attach to the given method of construction the proposition concerning the "transformation" of the polytropic curve.

If we substitute, in the formula for the computation of entropy

$$P = \int \frac{dQ}{AT},$$

the quantity of heat  $dQ = cdT$  according to equation (1), we get, by integration,

$$AP = AP_0 + c \log_e T, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where  $P_0$  represents the arbitrary constant of integration. If, for the initial condition,  $P_1$  is the entropy and  $T_1$  the temperature, there follows also

$$A(P - P_1) = c \log_e \frac{T}{T_1}, \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

and this expression is at the same time the equation for the transformation  $a'b'$  of the polytropic curve in question, provided  $P$  and  $P_1$  are laid off as abscissas and  $T$  and  $T_1$  as ordinates (Fig. 21b, p. 153); this is an equation which can also be written in the exponential form

$$T = T_1 e^{\frac{A(P - P_1)}{c}},$$

where  $e = 2.71828 \dots$ . The curve is the known logarithmic line (Logistik).

If we utilize equation (5) in equation (13a) and replace  $c$  by expression (4), we have

$$A(P - P_1) = (n - \kappa)c_v \log_e \frac{v_1}{v} \quad . \quad . \quad . \quad (13b)$$

and

$$A(P - P_1) = \left( \frac{n - \kappa}{n} \right) c_v \log_e \frac{p}{p_1} \quad . \quad . \quad . \quad (13c)$$

These formulas naturally embrace also all the special cases discussed above.

For heating under constant volume  $c = c_v$  and  $n = \infty$  must be substituted, and

for heating under constant pressure  $c = c_p$  and  $n = 0$ .

For a d i a b a t i c expansion  $c = 0$  and  $n = \kappa$ ; consequently according to equation (13a)  $P = P_1$  and the transformation of the adiabatic is therefore a straight line lying parallel to the axis of ordinates, as was mentioned before.

For i s o t h e r m a l and i s o d y n a m i c expansion  $c = \infty$  and  $n = 1$ ; the transformation is therefore a horizontal line.

If in any other case heat withdrawal is connected with an expansion, then  $P < P_1$  would result; in the transformation of the pressure curve  $ab$  (Fig. 21b) the positions of  $a'$  and  $b'$  would then be interchanged.

### § 32. PRESSURE CURVE OF GASES WHEN THE QUANTITY OF HEAT IS PROPORTIONAL TO THE CHANGE OF PRESSURE OR TO THE CHANGE OF VOLUME.

Although the preceding investigations of the polytropic curve discussed the most important cases and included those treated in the books on Physics, it seems appropriate to examine those cases in which the heat supplied to the gas is n o t proportional to the change of temperature, at least to discuss the pressure curves mentioned in the heading of this article.



Let the heat to be imparted be given by the expression

$$dQ = \frac{A}{\kappa - 1} [v_0 dp + \kappa p_0 dv], \quad . \quad . \quad . \quad . \quad (14)$$

and here let  $v_0$  and  $p_0$  be arbitrary constants which, in accordance with the notation introduced, represent any value whatever of a volume and of a pressure respectively.

If the values  $p_1$  and  $v_1$  correspond to the initial state of a gas, then integration of the preceding equation gives directly

$$Q = \frac{A}{\kappa - 1} [v_0(p - p_1) + \kappa p_0(v - v_1)]. \quad . \quad . \quad . \quad . \quad (14a)$$

The corresponding change of inner work follows from equation (52), p. 132,

$$U - U_1 = \frac{1}{\kappa - 1} [pv - p_1 v_1], \quad . \quad . \quad . \quad . \quad (14b)$$

and accordingly, with the help of the formula

$$Q = A(U - U_1 + L),$$

the external work becomes

$$L = \frac{1}{\kappa - 1} [v_0(p - p_1) + \kappa p_0(v - v_1) + p_1 v_1 - pv]. \quad . \quad . \quad (14c)$$

For the special case that the quantity of heat  $Q$  is proportional to the change of volume  $v - v_1$  we must place  $v_0 = 0$ ; on the other hand we would have to substitute  $p_0 = 0$  if the heat to be imparted is assumed to be proportional to the change of pressure  $p - p_1$ .

If we combined the foregoing equation (14) with the always valid equation (53c), p. 134, there follows

$$vdp + \kappa pdv = v_0 dp + \kappa p_0 dv,$$

and from this, by integration, we get the equation of the corresponding pressure curve:

$$(p - p_0)(v - v_0)^\kappa = (p_1 - p_0)(v_1 - v_0)^\kappa. \quad . \quad . \quad . \quad (15)$$

The curve is therefore related to the adiabatic; the coordinate axes of the latter are only shifted parallel an amount equal to  $v_0$  and  $p_0$ .

If for any value of  $v$  the pressure  $p$  has been computed from equation (15), the temperature  $T$  can be found from the equation of condition  $p v = B T$  for the point in question of the pressure curve, and then from one of the equations (55), p. 135, the corresponding value of the entropy  $P$ . But in so doing the way is also indicated for "transforming" the pressure curve in hand.

## II. Non-reversible Changes of State of Gases.

### § 33. EXPANSION OF GASES UNDER DIFFERENT CIRCUMSTANCES.

In the first section, § 15, the non-reversible process of any body was fully discussed; following those discussions, the propositions established can now be easily applied to the behavior of gases. Suppose a unit of weight of gas to be enclosed by a cylinder and its piston, and let volume  $v_1$ , pressure  $p_1$ , and temperature  $T_1$  correspond to the initial state represented by the point  $a_1$  (Fig. 25), and let this state be one of equilibrium and rest; then expansion of the gas will occur as soon as the pressure  $p_1$  acting from without on the piston  $K$  suddenly drops to the smaller value  $p_1'$ , and the work  $L'$ , which is thus given off to the outside by expansion to the volume  $v$ , is determined when (by the course of the pressure curve  $acb$ , the "working-pressure curve") the law is known according to which the counter-pressure  $p'$ , exerted from the outside upon the piston, varies during expansion.

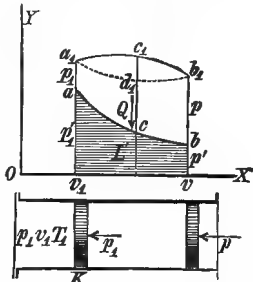


FIG. 25.

Now if, after attaining the volume  $v$ , the piston (supposed to be without weight) is suddenly held fast, then the gas, which has got into a condition of stormy motion, will gradually pass into the state of rest, and, after the state or condition of equilibrium is

established, the pressure of the gas will assume the value  $p$ , which corresponds to the point  $b_1$  of Fig. 25; corresponding to this point there is also a particular temperature  $T$ , which we will designate as the temperature of equilibrium, whose relation to  $p$  and  $v$  is given by the equation of condition of a gas. But similarly every intermediate point  $c$  of the working-pressure curve has a point at  $c_1$ , a certain pressure of equilibrium and a certain temperature of equilibrium, so that accompanying the working-pressure curve  $acb$  there is a second curve,  $a_1c_1b_1$ , which may be designated as the equilibrium-pressure curve (p. 76). If the temperature of equilibrium is known at the beginning and at the end, then according to equation (52a), p. 132, the quantity of heat consumed by the inner work is

$$A(U - U_1) = c_v(T - T_1),$$

and consequently we have for gases the quantity of heat  $Q'$  which must be supplied from without for this non-reversible process, according to equation (52), p. 132:

$$Q' = c_v(T - T_1) + AL', \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or, passing to the differential, we have

$$dQ' = c_v dT + Ap' dv, \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

and, taking account of equation (43), p. 124, and of the equation of condition, there follows finally

$$dQ' = \frac{A}{\kappa - 1} d(pv) + Ap' dv. \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

These equations are sufficient to solve problems of the proposed kind.

If the course of both pressure curves is known, the quantity of heat  $Q'$  can be determined; on the other hand, if the law of heat supply is known and one of the two pressure curves, then the course of the other can easily be determined. For the special case  $p' = p$  both curves coincide and the process is transformed into a reversible one.

We will apply the foregoing formulas to only one case, which, however, embraces an infinite number of cases, and just

those which have some technical interest. We assume that the heat imparted during the assumed non-reversible process is directly proportional to the change of the temperature of equilibrium; consequently  $dQ'$  is determined by the formula

$$dQ' = cdT, \quad . . . . . (2)$$

in which factor  $c$  is given as any constant quantity whatever, which may be designated as the specific heat for the proposed case; furthermore let the course of the working-pressure curve  $acb$  (Fig. 25) be given by equation

$$p'v^r = p_1'v^r, \quad . . . . . (3)$$

in which equation the exponent  $r$  likewise represents any constant quantity whatever, and possesses no relation to the first-mentioned quantity  $c$ .

Now the integration of equation (2) gives us at once the quantity

$$Q' = c(T - T_1), \quad . . . . . (4)$$

which is to be supplied during the assumed change, and by substitution in equation (1) there follows the external work  $L'$ ,

$$AL' = (c - c_v)(T - T_1). \quad . . . . . (5)$$

If we here substitute the temperature values in accordance with the relations given in equation (54), p. 134, and for the sake of brevity write

$$n = \frac{c - c_p}{c - c_v}, \quad . . . . . (6)$$

in which the new constant  $n$  is completely determined by  $c$ , then equation (5) also gives the work in the form

$$L' = \frac{1}{n-1}(p_1v_1 - pv). \quad . . . . . (5a)$$

But, on the other hand, on account of the changes of external pressure assumed in equation (3), we get from equation (7b), p. 154, for the external work, also

$$L' = \frac{1}{r-1}(p_1'v_1 - p'v), \quad . \quad . \quad . \quad . \quad (5b)$$

and therefore by equating the last two equations

$$pv = p_1v_1 + \frac{n-1}{r-1}(p'v - p_1'v_1) \quad . \quad . \quad . \quad . \quad (7)$$

for the sought equilibrium-pressure curve; by means of this there can be found the equilibrium-pressure curve  $p$  and the equilibrium-temperature  $T$  for every value of the volume  $v$ , because the initial values  $p_1$ ,  $v_1$ , and  $p_1'$  are supposed to be known, and  $p'$  is given by equation (3).

According to the choice  $c$  or  $r$ , or of  $n$  and  $r$ , we have before us an infinite number of special cases; the process is transformed into a reversible one when the two curves of working-pressure and of equilibrium-pressure coincide; in this case  $p_1' = p_1$  and  $p' = p$ , and from equation (7) there follows  $r = n$ ; then, if  $c$  is given, the constant  $r$  is no longer arbitrary, but bears a relation to  $c$  given by equation (6). We then have before us the polytropic curve which was treated above.

On the other hand, if, in the case under consideration, the two curves are not identical, then we are dealing with the non-reversible process, several special cases of which will be discussed.

CASE 1. The change takes place without heat being imparted or withdrawn. Here  $c=0$ , therefore according to equation (6)  $n=\kappa$ , and the equation of the equilibrium-pressure curve, which is here to be regarded as an adiabatic curve of the general kind, is written

$$pv = p_1v_1 + \frac{\kappa-1}{r-1}(p'v - p_1'v_1), \quad . \quad . \quad . \quad . \quad (7a)$$

in which formula we can substitute for  $p'$  its value derived from equation (3)

C a s e 2. If we assume  $r=0$ , then equation (3) gives  $p'=p_1'$ , the expansion of the gas takes place while overcoming the constant external pressure, and the equilibrium-pressure curve resulting from equation (7) is

$$pv = p_1v_1 - (n-1)p_1'(v-v_1). \quad . \quad . \quad . \quad (7b)$$

The curve is therefore an hyperbola. If this is not accompanied by a supply of heat, we must also make  $n=\kappa$ , and then

$$pv = p_1v_1 - (\kappa-1)p_1'(v-v_1). \quad . \quad . \quad . \quad (7c)$$

Finally if we assume the external pressure  $p_1'=0$ , that is, assume the expansion to take place without performance of outer work, we shall have

$$pv = p_1v_1;$$

consequently the equilibrium-pressure curve passes into an equilateral hyperbola; because of the equation of condition  $pv=BT$  and  $p_1v_1=BT_1$  the equilibrium-temperature appears as a constant quantity.

The latter case, whose numerical results might have been found in a shorter way directly from the fundamental equation (1), arises when the space filled with gas is put in communication with a vacuum. The expansion of the gas here takes place without the performance of external work, and experiments by J o u l e have in fact shown that the gas, after the expansion and passage into the condition of equilibrium, possesses the s a m e temperature as at the beginning of the experiment.

Let us once more return to the case given by equation (7c) for which there is expansion, under the constant external pressure  $p_1'$ , without supply of heat. As a limiting case we can assume the expansion to be continued so far that the final equilibrium-pressure  $p$  is equal to the external pressure  $p_1'$ ; with this case equation (7c) gives

$$\frac{v}{v_1} = \frac{p_1}{\kappa p} + \frac{\kappa-1}{\kappa},$$

from which the expansion ratio can be computed.

The ratio of the temperature values  $T$  and  $T_1$  can then be found from

$$\frac{T}{T_1} = \frac{1}{\kappa} + \frac{\kappa-1}{\kappa} \frac{p}{p_1},$$

and because  $n = \kappa$  the external work becomes, according to equation (5a),

$$L' = \frac{1}{\kappa-1} (p_1 v_1 - p v) = \frac{c_v}{A} (T_1 - T).$$

**Example.** If a kilogram [pound] of atmospheric air of the temperature  $t_1 = 15^\circ \text{C}$ . [ $59^\circ \text{F}$ .] expands, overcoming an external constant pressure of one atmosphere, at the same time expanding from the initial pressure of 2.5 atmospheres down to the terminal pressure of one atmosphere, then the foregoing formulas give

$$\frac{v}{v_1} = 2.064 \quad \text{and} \quad \frac{T}{T_1} = 0.8255.$$

Consequently  $T = 237.44$  or  $t = -35.56^\circ \text{C}$ . [ $T = 427.392^\circ \text{F}$ . or  $t = -32.008^\circ \text{F}$ .], and the external work

$$L' = 3612.2 \text{ mkg.} \\ [L' = 11851 \text{ ft-lb.}]$$

(Compare examples on pp. 138 and 141.)

Returning to the general case, represented by Fig. 25, the remark may not now be superfluous that the variable external pressure  $p'$  does not measure at the same time the gas-pressure itself during the non-reversible change; on account of the existing stormy and irregular motion of the gas particles during the process, neither the instantaneous pressure nor the corresponding temperature can be determined. The designations  $p$  and  $T$  used in the foregoing presentation refer expressly, we repeat, to the state of equilibrium and rest which ensues when the expansion is suddenly stopped at the volume  $v$ ; neither can the gradual passage, from the condition of stormy motion to the state of equilibrium at constant volume  $v$ , be followed more closely.

As regards the "transformation" of the non-reversible process discussed here, we can only refer to the general presentation in § 16 of the first section, p. 78; there we have simply to replace

the function  $S$  by the absolute temperature  $T$  and employ for the function

$$P = \int \frac{dQ}{AS} = \phi(p, v)^*$$

for gases, equations (55), p. 135; but the propositions enunciated in § 17, concerning the entropy of the non-reversible process of the kind before us as applied to gases, well deserve closer investigation.

According to equation (1a), p. 164, the quantity of heat  $dQ'$  for the non-reversible process is given by the expression

$$dQ' = c_v dT + A p' dv;$$

on the other hand, if the passage had taken place in reversible fashion along the equilibrium-pressure curve (Fig. 25), then the quantity of heat  $dQ$ , which is determined by

$$dQ = c_v dT + A p dv,$$

would have been needed.

The subtraction of the two equations gives

$$dQ' = dQ - A(p - p')dv,$$

and, if we divide both sides by  $AT$ , we get

$$\frac{dQ'}{AT} = \frac{dQ}{AT} - \frac{(p - p')dv}{T}.$$

The first term of the right-hand side is under all circumstances a complete differential, even when the change from the condition  $a_1$  to the state  $b_1$  has taken place, not along the equilibrium-pressure curve  $a_1c_1b_1$ , but along another reversible path ( $a_1d_1b_1$ , dotted in Fig. 25). The integration of the first term on the right-hand side is the change of entropy for the reversible passage and is found from equation (55a), p. 134,

$$P - P_1 = \frac{c_v}{A} \log_e \frac{pv^*}{p_1v_1^*}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$



The integral of the expression in the left member is, on the other hand, the change of entropy for the non-reversible process; we briefly designate this by  $P'$ , and if we substitute, as in equation (57), p. 81,

$$N = \int \frac{(p - p') dv}{T}, \quad . . . . . (9)$$

there follows

$$P' = P - P_1 - N. \quad . . . . . (10)$$

Now since the non-reversible process of the assumed kind permits of the integration indicated in equation (9), as soon as the course of the working-pressure and the equilibrium-pressure curve is known, we get through equation (10) the change  $P'$  of the entropy for this non-reversible process.

In illustration we use the case recently treated, a case shown to embrace an infinite number of special cases.

Consequently, heat is to be again imparted according to the law  $dQ' = cdT$ , and the course of the working-pressure curve is given by

$$p'v^r = p_1'v_1'^r,$$

where  $c$  and  $r$  are two constant quantities independent of each other.

Utilizing the equation of the equilibrium-pressure curve,

$$pv = p_1v_1 + \frac{n-1}{r-1}(p'v - p_1'v_1),$$

as given by equation (7), and using the relation

$$n = \frac{c - c_p}{c - c_v},$$

furnished by equation (6), we get, after some easily followed transformations, from equation (9) for the case before us:

$$AN = c_v \frac{\kappa - 1}{n - 1} \log_e \frac{pv^n}{p_1v_1^n}, \quad . . . . . (11)$$

accordingly we can compute from equation (10), with the help of equation (8), the change  $P'$  of entropy.

For example, if heat exchange does not take place so that  $c=0$  and  $n=\kappa$ , we get

$$AN = c_v \log_e \frac{pv^\kappa}{p_1v_1^\kappa}$$

and

$$P' = 0.$$

On the other hand if  $r=0$ , then  $p'=p_1'$ , and if in addition  $p'=p_1'=0$ , that is, if the expansion takes place without the performance of outer work, then  $pv=p_1v_1$  for the equilibrium-pressure curve, and consequently, according to equation (11),

$$AN = c_v(\kappa-1) \log_e \frac{v}{v_1}.$$

Further pursuit of the non-reversible process before us is of purely theoretical interest only.

### § 34. MIXTURES OF DIFFERENT GASES.

The heat equations (53), p. 134, were developed under the hypothesis that we were dealing with the unit of weight of gas, but if we now assume that there is included in a space of  $V$  cbm. [cu. ft.]  $G$  kg. [lb.] of gas of the pressure  $p$ , temperature  $T$ , and the specific volume  $v$ , we first have the relation

$$V = Gv,$$

and in order to determine the quantity of heat  $dQ$ , which the weight  $G$  of the gas needs for an infinitesimal reversible change of state, we must employ the following identical equations which follow from equations (53), p. 134, when we multiply their right members by  $G$ :

$$dQ = \frac{A}{\kappa-1} d(Vp) + A p dV \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

$$= c_v G dT + A p dV \quad . \quad . \quad . \quad . \quad . \quad (12b)$$

$$= \frac{A}{\kappa-1} [V dp + \kappa p dV] \quad . \quad . \quad . \quad . \quad . \quad (12c)$$

$$= c_v G \left[ dT + (\kappa-1) T \frac{dV}{V} \right] \quad . \quad . \quad . \quad . \quad (12d)$$

$$= c_p G \left[ dT - \frac{\kappa-1}{\kappa} T \frac{dp}{p} \right] \quad . \quad . \quad . \quad . \quad (12e)$$

Let us now suppose that a space  $V$  is filled with two different gases, say with  $G_1$  kg. [lb.] of the one (a) and  $G_2$  kg. [lb.] of the second (b). Let the specific heats at constant volume be respectively  $c_v'$  and  $c_v''$ , at constant pressure  $c_p'$  and  $c_p''$ , and the corresponding ratio of these two specific heats be  $\kappa'$  and  $\kappa''$ ; furthermore at the common temperature  $T$  of the mixture,  $p'$  will be the pressure of gas a, and  $p''$  that of gas b, so related that the sum  $p' + p''$  represents the total pressure  $p$ .

If we now supply the quantity of heat  $dQ$  to this mixture, there follows from equation (12b)

$$dQ = (c_v' G_1 dT + A p' dV) + (c_v'' G_2 dT + A p'' dV),$$

or, if we collect the corresponding terms and represent the total weight  $G_1 + G_2$  of both quantities of gas by  $G$ , and remember that  $p = p' + p''$ , we will get

$$dQ = G \left( \frac{c_v' G_1 + c_v'' G_2}{G_1 + G_2} \right) dT + A p dV.$$

Comparison of this expression with equation (12b) shows that so far as heat supply is concerned the mixture behaves exactly like a single gas, whose specific heat  $c_v$  at constant volume is determined by

$$c_v = \frac{c_v' G_1 + c_v'' G_2}{G_1 + G_2}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In exactly the same way when equation (12d) is employed we find for the mixture the specific heat at constant pressure

$$c_p = \frac{c_p' G_1 + c_p'' G_2}{G_1 + G_2}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and for the ratio of the two specific heats of the mixture

$$\kappa = \frac{c_p}{c_v} = \frac{c_p' G_1 + c_p'' G_2}{c_v' G_1 + c_v'' G_2}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and for the differences of these specific heats

$$c_p - c_v = \frac{(c_p' - c_v')G_1 + (c_p'' - c_v'')G_2}{G_1 + G_2} \quad \dots \quad (16)$$

Suppose the mixture to be composed of more than two gases,<sup>1</sup> then we can write for the mixture, in general fashion:

$$c_v = \frac{\Sigma(c_v G)}{\Sigma(G)}, \quad \dots \quad (13a)$$

$$c_p = \frac{\Sigma(c_p G)}{\Sigma(G)}, \quad \dots \quad (14a)$$

$$\kappa = \frac{\Sigma(c_p G)}{\Sigma(c_v G)}, \quad \dots \quad (15a)$$

$$c_p - c_v = \frac{\Sigma[(c_p - c_v)G]}{\Sigma(G)}. \quad \dots \quad (16a)$$

From the relation  $c_p - c_v = AB$ , derived from equation (42), p. 124, and when  $B_m$  is the constant for the equation of condition for the mixture, and similarly  $B_1$ ,  $B_2$ , etc., for the separate gases, there follows according to equation (16a)

$$B_m = \frac{\Sigma(GB)}{\Sigma(G)},$$

as was already expressed by equation (19a), p. 110. According to the equations there shown the pressures of the separate gases of the mixture are

$$\frac{p'}{p} = \frac{G_1 B_1}{\Sigma(GB)}, \quad \frac{p''}{p} = \frac{G_2 B_2}{\Sigma(GB)}, \quad \text{etc.} \quad \dots \quad (17)$$

After these preparations the mixing of two separate kinds of gases can be closely followed; the operation is not a reversible one.

Let us suppose two spaces  $V_1$  and  $V_2$  (Fig. 26) separated by

<sup>1</sup> Some writers designate the product  $Gc_v$  and  $Gc_p$ , of the weight of the gas by the corresponding specific heat, as "calorific capacity for constant volume and for constant pressure respectively." The equations of the text then enunciate that the calorific capacity of the mixture is equal to the sum of the calorific capacities of the separate parts before the mixture.

a partition  $ab$ ; suppose that in one space there exists  $G_1$  kg. [lb.] of pressure  $p_1$  and temperature  $T_1$ , and that there are in the other space  $G_2$  kg. [lb.] of another gas having the pressure  $p_2$  and the temperature  $T_2$ ; if the partition  $ab$  is removed there is a mixture

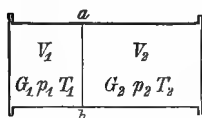


FIG. 26.

of the two gases, and the question now is as to the character of the mixture, its pressure  $p$  and temperature  $T$ . Let us here assume that during the process of mixing heat is neither supplied nor withdrawn, and that therefore before and after the mixture the total

heat contents of the two gases is the same; but we must also assume, what is decisive for the following developments, that the partition  $ab$  is so removed that the two kinds of gases are perfectly free to diffuse and expand. Very different conditions would exist if the partition had an aperture through which the gas, in the space having the higher pressure, could flow into the other space, a case which will receive full consideration later on.

According to equation (52b), p. 133, the heat contents, or the gas heat in the unit of weight of a gas at temperature  $T$ , is

$$J = J_0 + c_v T,$$

when  $J_0$  is a constant corresponding to the particular gas in question. This constant quantity is, to be sure, not known for the different gases, either as regards absolute value or as regards its ratio to the value of any particular gas, say to hydrogen, but in a mechanical mixture, as is assumed in the case before us, this circumstance causes no difficulty. If we designate the constant for the mixture by  $J_0$ , the one for the gas in the space  $V_1$  by  $J_0'$ , and for the other space by  $J_0''$ , and if  $c_v$ ,  $c_v'$ , and  $c_v''$  mean the specific heats at constant volume, then before the mixture the heat content  $J_m$  of the two spaces is

$$J_m = (G_1 J_0' + c_v' G_1 T_1) + (G_2 J_0'' + c_v'' G_2 T_2);$$

on the other hand after the mixture the heat in the two spaces is

$$J_m = G J_0 + c_v G T,$$

provided the total weight  $G_1 + G_2$  is designated by  $G$ .

By equating both expressions we get the total heat contents  $J$  of a unit of weight of the mixture: \*

$$J = J_0 + c_v T = \frac{G_1 J_0' + G_2 J_0''}{G_1 + G_2} + \frac{c_v' G_1 T_1 + c_v'' G_2 T_2}{G_1 + G_2}.$$

From this follows the constant  $J_0$  for the mixture,

$$J_0 = \frac{G_1 J_0' + G_2 J_0''}{G_1 + G_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and if we utilize equation (13) we get for the mixing temperature

$$T = \frac{c_v' G_1 T_1 + c_v'' G_2 T_2}{c_v' G_1 + c_v'' G_2}. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From the equation of condition for gases  $pv = BT$ , from  $Gv = V$  and the relation (54), p. 135, we have

$$c_v GT = \frac{AVp}{\kappa - 1},$$

and from this and equation (19), also

$$\frac{Vp}{\kappa - 1} = \frac{V_1 p_1}{\kappa' - 1} + \frac{V_2 p_2}{\kappa'' - 1}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

from which formula the pressure  $p$  of the mixture can be directly computed. It is worthy of note that in equation (19) we can write, in place of the absolute temperature, the temperature according to Celsius [Fahrenheit], that is, write

$$t = \frac{c_v' G_1 t_1 + c_v'' G_2 t_2}{c_v' G_1 + c_v'' G_2}. \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

We moreover recognize that the preceding formulas can easily be written for the case in which we have to do with the mixture of more than two gases.

If we assume that the two gases to be mixed are of the same

constitution, then  $c_v' = c_v'' = c_v$ , and  $\kappa' = \kappa'' = \kappa$ , and then the mixture's temperature is

$$T = \frac{G_1 T_1 + G_2 T_2}{G_1 + G_2}, \quad . \quad . \quad . \quad . \quad . \quad (19b)$$

and the formula for computing the pressure of the mixture is

$$Vp = V_1 p_1 + V_2 p_2, \quad . \quad . \quad . \quad . \quad . \quad (20a)$$

two equations of which much use has been made, of the former in Physics and of the other in technical investigations.

On the other hand if different gases are mixed, and if their temperature is the same before the mixture,  $t_1 = t_2$ , then equation (19a) also gives  $t = t_1$ ; consequently after the mixture has been effected (after the condition of equilibrium is established) the temperature of the mixture is equal to that before the mixture.

Finally, if the two gases before the mixture have different temperatures but equal pressures, so that  $p_1 = p_2$ , then equation (20) shows that the mixture's pressure  $p$  is only identical with the initial pressure when  $\kappa' = \kappa''$ , a case which exists for the simple gases.

As a special example we will consider the mixture of hydrogen and oxygen in the ratio necessary to form detonating gas.

Therefore if in the one space  $V_1$  (Fig. 26) there exists  $G_1$  kg. [lb.] of hydrogen, and in the other  $G_2 = 8 G_1$  kg. [lb.] of oxygen, and if we assume each to have the same pressure and the same temperature  $T$ , then, according to the preceding propositions, the temperature and the pressure of the mixture known as detonating gas will remain the same as before the mixture.

Since  $c_v' = 2.4123$  for hydrogen and  $c_v = 0.1551$  for oxygen (table, p. 126), there results for the mixture (detonating gas) the specific heat  $c_v$  according to equation (13):

$$c_v = 0.4059.$$

If  $J_0'$  is the constant in equation (52b), p. 133, for the heat contents of hydrogen, and  $J_0''$  that for oxygen, which values, to

be sure, are still unknown, then the corresponding constant for detonating gas is given by equation (18):

$$J_0 = \frac{1}{9}J_0' + \frac{8}{9}J_0'', \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and the heat contents of detonating gas at temperature  $T$  and pressure  $p$  is accordingly

$$J = J_0 + c_v T,$$

in which equation the foregoing values of  $J_0$  and  $c$  must be substituted.

Now if we suppose, in order to pursue the case somewhat farther, that the detonating gas explodes (say by an electric spark) at constant volume, the vapor of water will be formed with heat development and a great rise of temperature. If from this steam at constant volume we withdraw the quantity of heat  $Q$  in order to reduce it to the initial temperature  $T$  of the detonating gas, then the heat contents of the steam at the temperature  $T$  will be given by

$$J_0''' + c_v''' T = J_0 + c_v T - Q,$$

when  $c_v'''$  represents the specific heat of steam at constant volume, and  $J_0'''$  the heat contents, according to equation (52b), p. 133.

From the preceding equation there can be determined for the unit of weight of detonating gas the quantity of heat  $dQ$  developed by the explosion:

$$Q = (J_0 - J_0''') + c_v - c_v''' T. \quad . \quad . \quad . \quad (15g)$$

$Q$  therefore appears as dependent upon the temperature  $T$ , at which the chemical combination of the two gases was permitted, a proposition which was also discovered by Kirchhoff<sup>1</sup> for the case before us.

<sup>1</sup> Poggendorff's Annalen, Vol. 103, p. 205; compare also C. Neumann, "Vorlesungen über die mechanische Theorie der Wärme," 1875, p. 175.



The equation of condition for detonating gas was given in § 20, p. 115, as  $pv = \frac{1}{8}B_0T$ ; the steam formed from the detonating-gas on the other hand had, for the same temperature  $T$  and the same volume, a pressure  $p'$  determined from the equation of condition  $p'v = \frac{1}{8}B_0T$  (§ 20, p. 116); in the present case, therefore, the final pressure of the steam is  $p' = \frac{2}{3}p$ .

The foregoing results of course only hold when it may be assumed that the equation of condition for steam is the same as for gases.

### § 35. FLOW OF A GAS FROM ONE VESSEL INTO ANOTHER FOR CONSTANT VESSEL-VOLUMES.<sup>1</sup>

Let two vessels  $A$  and  $B$  (Fig. 27) be connected by a pipe provided with a cock  $F$ , and let both vessels be filled with one and the same kind of gas, say atmospheric air. In vessel  $A$ , whose volume is  $V_1$ , there will be at the beginning (with closed valve)  $G_1$  kg. [lb.] of air having the pressure  $p_1$ , specific volume  $v_1$ , and temperature  $T_1$ ; the other vessel,  $B$ , which we will regard as the receiving vessel, has the volume  $V_2$ , and contains  $G_2$  kg. [lb.] of air of pressure  $p_2$ , volume  $v_2$ , and temperature  $T_2$ . We will suppose both vessels to be impenetrable to heat, consequently the occurrence to be considered must take place without heat being supplied to, or withdrawn from, the outside.

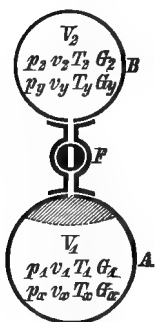


FIG. 27.

Suppose the cock  $F$  to be open for a time, then after it is closed, provided  $p_1 > p_2$ , there will remain behind in the space  $A$  a weight of air  $G_x$ , and therefore the quantity of air  $G_1 - G_x$  will have passed into the receiver  $B$ . This vessel  $B$  now contains the weight of air  $G_y = G_1 + G_2 - G_x$ ; after the efflux let pressure, volume, and temperature of the gas in the discharging vessel  $A$  be  $p_x$ ,  $v_x$ , and  $T_x$ , in the receiving vessel  $B$  on the other hand be  $p_y$ ,  $v_y$ , and  $T_y$ .

<sup>1</sup> The problem here specified was first solved by Bauschinger in an excellent article entitled "Theorie des Ausströmens vollkommener Gase aus einem Gefäß und ihres Einströmens in ein solches," published in Schlämilch's Zeitschrift für Mathematik und Physik, Vol. VIII, p. 81.

If the quantity of gas  $G_x$ , remaining behind, is regarded as given, the problem will be to determine the just-mentioned six magnitudes; but because three of them are related to each other by

$$p_x v_x = BT_x \quad \text{and} \quad p_y v_y = BT_y,$$

only four equations must be set up for the solution of the problem, and let us assume that the unknown quantities to be determined are the pressures  $p_x$  and  $p_y$  and the temperatures  $T_x$  and  $T_y$ .

To be sure the determination of these values assumes that, after the closing of the cock, the condition of equilibrium has been restored in each of the two spaces, for during the flow and at the instant of closing there exists a disturbance of equilibrium: the gas will be in stormy, eddying, motion, and the disturbance will be greater the smaller the contents of the two vessels and the greater the aperture through which the flow takes place. The expansion which occurs in the discharging vessel and the expansion which occurs in the receiving vessel are neither of them reversible, but if we assume a still smaller aperture of flow and large contents for the vessels we can assume that the expansion and compression take place in reversible fashion. The gas flowing toward the orifice will move in a funnel-shaped space and will diffuse itself similarly in the receiving vessel; the contents of the two funnels, and therefore of the weight of the gas moving in them, can, under the assumption made, be regarded as very small in comparison with the remaining gas mass which is at rest in the two spaces, and can therefore be neglected. In this case the values  $p_x$  and  $p_y$  are the equilibrium pressures, and  $T_x$  and  $T_y$  the equilibrium temperatures, which already exist at the instant of closing the cock; under the assumption made it is not even necessary to think of the closing of the cock, and it may be assumed that the pressures  $p_x$  and  $p_y$ , experimentally found by observing a manometer, represent the equilibrium pressure in the two vessels during the flow.

If the valve is kept open till the pressure in both vessels has become equal, that is, till the flow originating from the difference of pressure is ended, then the temperatures in the two vessels will

still be different, and not until the aperture of flow is kept open for quite a period will equalization of temperatures by diffusion obtain; when it occurs the conditions will be of the sort discussed in the preceding article.

Under these limiting assumptions, part of which will be dropped in subsequent investigations, the occurrences can easily be followed by calculation in the following manner.

#### (a) Occurrences in the Discharging Vessel.

Let the hatched part of Fig. 27 (p. 177), enclosed by the dotted line, represent the space occupied, before the opening of the valve, by the quantity of gas discharged up to the moment of closing the cock, then the remaining gas quantity  $G_x$  originally possessed the volume  $V_x = G_x v_1$ , which is shown in Fig. 27 by that part of the contents of the vessel that is not hatched. This quantity of the gas now expands in reversible adiabatic fashion to the vessel volume

$$V_1 = G_x v_x = G_1 v_1.$$

From this we can now find the specific volume  $v_x$ , of the gas remaining behind when the orifice is closed:

$$\frac{v_x}{v_1} = \frac{G_1}{G_x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and hence according to equation (60), p. 140, can be found the pressure  $p_x$  from the equation

$$\frac{p_x}{p_1} = \left( \frac{G_x}{G_1} \right)^\kappa, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and from equation (61), p. 140, the temperature  $T_x$  is given by

$$\frac{T_x}{T_1} = \left( \frac{p_x}{p_1} \right)^{\frac{\kappa-1}{\kappa}} = \left( \frac{G_x}{G_1} \right)^{\kappa-1} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If we provide the discharging vessel with a manometer we can easily observe the pressure  $p_x$  at the instant of closing the

orifice or in the case of continuous flow, at any time intervals; according to equation (26) we can compute, for every observed quantity of air  $G_x$  remaining behind, the weight of air which flows out in the several intervals of time. Equations (23) and (25) then give the specific volume  $v_x$  and the temperature  $T_x$  of the quantity of air remaining behind in the discharging vessel at the end of each interval.

(b) Occurrences in the Receiving Vessel.

The total heat content of the gases in the two vessels taken together is, according to the presentation in the preceding articles, at the beginning of the experiment,

$$(G_1 + G_2)J_0 + c_v(G_1T_1 + G_2T_2);$$

on the other hand at the end of the flow, after the close of the orifice or at any instant during the flow, the total heat is

$$(G_x + G_y)J_0 + c_v(G_xT_x + G_yT_y).$$

Both expressions are equal, for during the operation heat is neither supplied nor rejected, and because we also have

$$G_y + G_x = G_1 + G_2, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

we will get the equation

$$G_yT_y + G_xT_x = G_1T_1 + G_2T_2. \quad . \quad . \quad . \quad . \quad . \quad (27)$$

From this formula we can now compute the temperature  $T_y$ , for an already given quantity  $G_x$ , because  $G_y$  is known to us from equation (26) and  $T_x$  from equation (25). By substituting the value  $T_x$  we get, directly,

$$G_yT_y = G_2T_2 + G_1T_1 \left[ 1 - \left( \frac{G_x}{G_1} \right)^\kappa \right]. \quad . \quad . \quad . \quad . \quad (27a)$$

If we multiply both sides by the constant  $B$  of the equation of condition of the gas, there follows, on account of the relations

$$V_2 = G_yv_y = G_2v_2 \quad \text{and} \quad V_1 = G_xv_x = G_1v_1,$$

the pressure  $p_y$  in the receiving vessel

$$p_y = p_2 + \frac{V_1 p_1}{V_2} \left[ 1 - \left( \frac{G_x}{G_1} \right)^{\kappa} \right], \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and, provided the pressure  $p_x$  has been computed or observed, we also have, from equation (24),

$$V_1 p_x + V_2 p_y = V_1 p_1 + V_2 p_2. \quad . \quad . \quad . \quad . \quad (28a)$$

At the end of the flow  $p_x = p_y = p$ , therefore,

$$p = \frac{V_1 p_1 + V_2 p_2}{V_1 + V_2}. \quad . \quad . \quad . \quad . \quad . \quad (28b)$$

Then with the help of this value we can easily compute the quantity of gas transferred, the temperature in the discharging vessel and in the receiving vessel, quantities which, to be sure, are only valid for one instant because diffusion begins immediately after the equalization of pressure.

The equations of the preceding problem furnish a basis for the treatment of a series of important special cases, of which a few, possessing scientific interest and which have occasioned special experimenting, will be discussed.

### § 36. FLOW OF FREE ATMOSPHERIC AIR INTO A VESSEL.

Let us assume that the cubic capacity  $V_1$  of the discharging vessel  $A$  (Fig. 27, p. 178) is infinitely large, therefore  $G_1 = \infty$ . This case exists when free atmospheric air flows into a vessel which contains rarefied air at the beginning;  $p_1$  is then the atmospheric pressure, and  $T_1$  the temperature of the external air; the initial temperature in the receiving vessel, say in the receiver of an air-pump, may have any value  $T_2$  whatever.

To solve the problem it is well to subject the corresponding formulas of the preceding articles to a transformation; let  $G$  designate the weight of gas which, in a given time, has passed from one vessel into the other, then we must substitute in the formerly

given equations  $G_x = G_1 - G$  and  $G_y = G_2 + G$ ; hence, for the discharging vessel, we have, according to equations (24) and (25),

$$\frac{p_x}{p_1} = \left(1 - \frac{G}{G_1}\right)^\kappa \quad \text{and} \quad \frac{T_x}{T_1} = \left(1 - \frac{G}{G_1}\right)^{\kappa-1}.$$

Both formulas give for the present case,  $G_1 = \infty$ ,

$$p_x = p_1 \quad \text{and} \quad T_x = T_1,$$

a result that is self-evident.

On the other hand for the changes in the receiving vessel equation (27a) gives

$$(G_2 + G)T_y = G_2T_2 + G_1T_1 \left[1 - \left(1 - \frac{G}{G_1}\right)^\kappa\right].$$

If we develop the exponential term according to the binomial theorem, that is, put

$$\left(1 - \frac{G}{G_1}\right)^\kappa = 1 - \kappa \frac{G}{G_1} + \frac{\kappa(\kappa-1)}{1.2} \left(\frac{G}{G_1}\right)^2 - + \dots,$$

there follows

$$(G_2 + G)T_y = G_2T_2 + \kappa GT_1 - \frac{\kappa(\kappa-1)}{1.2} \frac{G_2T_1}{G_1} + \dots,$$

and from this we get for  $G_1 = \infty$  the temperature  $T_y$  in the vessel after flow of  $G$  kg. [lb.] of the external atmospheric air into the vessel:

$$T_y = \frac{G_2T_2 + \kappa GT_1}{G_2 + G}. \quad \dots \dots \dots (29)$$

Multiplying both sides of the equation by the constant  $B$  of the equation of condition, there follows, after some easily made transformations, the pressure  $p_y$  at the end of the influx

$$p_y = p_2 + \frac{c_p(\kappa-1)GT_1}{AV_2}, \quad \dots \dots \dots (30)$$

and also

$$p_y = p_2 \left[1 + \frac{\kappa GT_1}{G_2T_2}\right]. \quad \dots \dots \dots (30a)$$

From equation (29), which can also be written in the form

$$T_y = T_2 + \frac{(\kappa T_1 - T_2)G}{G_2 + G}, \quad . \quad . \quad . \quad . \quad . \quad (29a)$$

we see that a rise of temperature is connected with the influx into the chamber.

A very remarkable result is reached, and Bauschinger (ibid.) has already called attention to it, if we assume that the space into which the outer atmospheric air flows is empty (is a vacuum) at the beginning. Equation (30) gives in this case, for  $p_2=0$  and  $G_2=0$ ,

$$p_y = \frac{c_p(\kappa - 1)GT_1}{AV_2}, \quad . \quad . \quad . \quad . \quad . \quad (30b)$$

and equation (29) furnishes

$$T_y = \kappa T_1. \quad . \quad . \quad . \quad . \quad . \quad (29b)$$

From the last equation follows, that at the entrance of the atmospheric air into a vacuum, from the first instant of opening the orifice, the temperature there rises suddenly up to the value  $\kappa T_1$ , and then remains constant as long as the influx into the vessel (assumed to be impenetrable to heat) lasts. If we replace the absolute temperature in equation (29b) by the temperature according to Celsius (Fahrenheit), there follows

$$\begin{aligned} t_y &= 111.93 + \kappa t_1 \\ [t_y &= 188.354 + \kappa t_1]. \end{aligned}$$

Consequently if the external atmospheric air had the temperature  $t_1=15^\circ$  ( $59^\circ$ ), there would result  $t_y=133.08^\circ$  ( $271.544^\circ$  F.).

If the vessel is not initially a vacuum, but is brought before the flow of the air into it, by suitable heating from the outside, up to the temperature  $T_2=\kappa T_1$ , then equation (29a) gives  $T_y=T_2$ ; but the temperature of the air in the vessel maintains itself at the constant heat  $T_2$  during the influx. When the pressure  $p_y$  has become equal to the external pressure  $p_1$ , the influx is ended;

at this instant the air entered, according to equation (30a), amounts to

$$G = \frac{(p_1 - p_2)G_2T_2}{\kappa p_2T_1} = \frac{V_2(p_1 - p_2)}{\kappa BT_1},$$

and substitution in equation (29) gives the temperature in the vessel

$$T_y = \frac{\kappa T_1 T_2 p_1}{p_1 T_2 + p_2 (\kappa T_1 - T_2)}.$$

A corresponding experiment cannot, to be sure, be realized, as will now be more fully shown. But equations (29) and (30) are of historical interest. As regards the latter equation there can be computed from it

$$G = \frac{AV_2(p_y - p_2)}{c_p(\kappa - 1)T_1}, \quad . \quad . \quad . \quad . \quad . \quad (31)$$

or, if we put, in place of the weight  $G$  of the air which has entered, its volume  $V$  measured at the external pressure  $p_1$ , taking account in so doing of the relation  $Vp_1 = GBT_1$ , and determining the constant  $B$  from equation (54), p. 134, we get

$$V = \frac{V_2(p_y - p_2)}{\kappa p_1}. \quad . \quad . \quad . \quad . \quad . \quad (31a)$$

Therefore if we provide the receiver of an air-pump with a manometer and with an orifice through which atmospheric air can enter, and observe during influx the manometer reading  $p_y$  at stated intervals of time, then according to the preceding formulas we can compute the weight of air  $G$  or the volume of air  $V$ , measured at the external pressure  $p_1$ , which passes through the orifice during the separate intervals. In this way a method may be established of determining experimentally the quantity of air flowing through a given orifice in a unit of time for a given difference of pressure, and the values thus found can be compared with the theoretical results of investigations on the efflux of air through orifices.



This way was in fact pursued by de Saint-Venant and Wantzel<sup>1</sup> (1839); they allowed atmospheric air to flow through different kinds of circular orifices, whose diameters were  $\frac{2}{3}$ , 1, and 1.5 mm. [0.02624, 0.03937, and 0.05906 in.], into the receiver of an air-pump whose cubic capacity to be sure was only 0.0174 cbm. [0.615 cu. ft.], in which there was generally at the beginning of the various experimental series a pressure of 10 to 20 mm. (0.3937 to 0.7874 in.) of mercury. The investigators in one experimental method allowed the air to flow uninterruptedly till the pressure was equalized, and observed at equal intervals of time (every 5 seconds) the increment of pressure; in the second method they allowed the air to flow in with interruptions, after each period of 5 seconds the orifice was closed for a few seconds with the finger and the pressure immediately noted.

The work of de Saint-Venant and Wantzel remained almost unnoticed for thirty years; doubtless this was due to the circumstance that it was Poncelet who declared in his report to the Paris Academy that the experiments were not decisive because they were conducted on too small a scale (with too small orifices); one must agree with this judgment, but must add that neither could the results of the then given experiments be regarded as reliable. During the development of the above formulas it was assumed that the receiving as well as the discharging vessel was impermeable to heat, a condition that cannot be satisfied because during the influx into the receiver a marked rise of temperature occurs there, in consequence of which the air in the interior gives off heat through the walls of the vessel to the external atmosphere during the whole duration of the experiment; consequently in the first experimental method the increment of pressure  $p_y - p_2$  takes place to a less degree than is assumed in equations (31) and (31a). In the second method, to be sure, it was assumed that on account of the short period of influx (5 seconds) the loss of heat by radiation might be neglected;

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<sup>1</sup> "Mémoire et expériences sur l'écoulement de l'air, déterminé par des différences de pressions considérables," by Barré de Saint-Venant and Laurent Wantzel. (Presented to the Academy of Sciences, Feb. 25, 1839.) Journal de l'École polytechnique, XVI, 1839.

but the experimenters should have closed the orifice not only for a few seconds but till there had been complete equalization of temperature with the external atmosphere.

The beginning of influx ought to be permitted only when the initial temperature  $T_2$  in the vessel is identical with the external temperature  $T_1$ , which can be recognized when the manometer reading for the closed vessel keeps constant.

Now for the beginning of the experiment we have the relation  $V_2 p_2 = G_2 B T_1$ , and for the end, after  $G$  kg. [lb.] air have entered, we have  $V_2 p = (G_2 + G) B T_1$ , provided equalization of temperature has taken place and the manometer reading has become stationary at the pressure  $p$ ; a combination of the two equations then gives for the quantity of air entered

$$G = G_2 \frac{(p - p_2)}{p_2}, \quad . . . . . (32)$$

or, if we measure the quantity of air  $G$  in cubic meters (cu. ft.) at external pressure,

$$V = V_2 \frac{(p - p_2)}{p_1} \quad . . . . . (32a)$$

There are therefore two ways of determining the quantity of air admitted, either with the help of equations (31) and (31a), by reading the pressure  $p_y$  in the vessel at the instant of closing, or with the help of the preceding equations (32) and (32a) by observing the pressure  $p$  at the end after equalization of temperature; the latter procedure is evidently the more reliable one.

De Saint-Venant and Wantzel of course did not know equations (31), which are derived from the laws of thermodynamics, but calculated the air volume  $V$  according to equation (32a), and in so doing committed the error of not waiting for the equalization of temperature by substituting  $p_y$  in the formula instead of  $p$ .

In spite of these defects, however, their article is of high value, for the authors have developed laws concerning the efflux of gases to which men have recently returned and which will be discussed more fully below.

The foregoing computations are of interest also for other reasons; the behavior of the two equations (31a) and (32a) gives

$$\kappa = \frac{p_y - p_2}{p - p_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Therefore if we allow air to flow into a vessel in which there is rarefied atmospheric air of the pressure  $p_2$  and of the temperature of the external atmosphere, and if we observe the pressure  $p_y$  at the instant of closing the orifice, and also observe the pressure  $p$  after equalization of temperature, then the preceding equation furnishes us with the means of determining the important physical constant  $\kappa$ .

If the vessel is a vacuum at the beginning, that is if  $p_2 = 0$ , we get still more simply

$$\kappa = \frac{p_y}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (33a)$$

In this way, corresponding to equation (33), Clément and Desormes determine the value  $\kappa$ . Of course to safely assume that there is no heat exchange of the gas with the walls of the vessel during the influx depends on the influx orifice being open only a very short time. However, this condition is hard to satisfy; the walls of the vessel have the external temperature  $T_1$ , the entering air has, according to equation (29a), a higher temperature after expansion (spreading), and because it comes in contact with the cooler walls during its stormy motion, the consequent lowering of temperature will cause the observed temperature  $p_y$  to be read too small and hence it will turn out smaller than was expected, and this, in fact, is what occurred in the experiments of Clément and Desormes. By the method given, therefore, a reliable determination of the important magnitude is not to be expected, and of this the author has convinced himself by recent experiments conducted on a large scale.

### § 37. FLOW OF AIR FROM THE VESSEL INTO THE FREE ATMOSPHERE.

If air flows into the free atmosphere from a vessel impermeable to heat and possessing the volume  $V_1$ , in which there exists at the beginning the pressure  $p_1$ , the temperature  $T_1$ , and  $G_1$  kg. (lb.) of air, then after a certain time the pressure will fall to  $p_x$  and the temperature to  $T_x$ . If at this instant the orifice is closed and if  $G_x$  is the weight of air remaining behind in the vessel, then there exist between these quantities the relations given by equations (24) and (25), p. 180. If  $G$  is the weight of air discharged, we must put  $G_x = G_1 - G$ , and equation (24) gives for the assumptions there made (r e v e r s i b l e adiabatic expansion of air in the discharging vessel during efflux):

$$G = G_1 \left[ 1 - \left( \frac{p_x}{p_1} \right)^{\frac{1}{\kappa}} \right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

If we designate by  $p_2$  and  $T_2$  the pressure and temperature of the external atmosphere, which do not undergo any change during the experiment, and assume beforehand that the temperature of the air in the vessel is originally identical with that of the external atmosphere, so that  $T_1 = T_2$ , then, according to equation (25),

$$\frac{T_x}{T_2} = \left( \frac{p_x}{p_1} \right)^{\frac{\kappa-1}{\kappa}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Consequently if we observe with the help of a manometer the initial pressure  $p_1$  and the terminal pressure  $p_x$ , at the instant of closing of the orifice, then by equation (34) the quantity of air can be computed which attains efflux, and by equation (35) the temperature  $T_x$  at the instant of closing.

If we wish to measure the quantity of air discharged in cubic meters under the initial inner pressure  $p_1$ , and under the initial temperature  $T_2$ , and designate this volume by  $V$ , we have the relation

$$V p_1 = G B T_2.$$

In like manner the weight  $G_1$  is determined from the relation  $V_1 p_1 = G_1 B T_2$ ; the use of these two formulas in equation (34) also gives

$$V = V_1 \left[ 1 - \left( \frac{p_x}{p_1} \right)^{\frac{1}{\kappa}} \right] \dots \dots \dots (34a)$$

If we drop the assumption that the vessel is impenetrable to heat, then from the moment of closing the orifice, and because  $T_x < T_2$ , the external atmospheric air will give off heat to the air remaining behind in the vessel till the temperature there has risen to the initial value  $T_2$ ; in doing this the pressure  $p_x$  rises to the pressure  $p$ , which finally is stationary and can easily be observed, provided we wait long enough when making the experiment. This heating takes place under constant volume, and therefore with the assumed notation we have the relations

$$V_1 p_x = (G_1 - G) B T_x \quad \text{and} \quad V_1 p = (G_1 - G) B T_2,$$

from which follows

$$\frac{T_x}{T_2} = \frac{p_x}{p} = \frac{p_x}{p_1} \cdot \frac{p_1}{p} \dots \dots \dots (36)$$

The combination of this equation with equation (35) gives

$$\left( \frac{p_x}{p_1} \right)^{\frac{1}{\kappa}} = \frac{p}{p_1}, \quad \dots \dots \dots (37)$$

and if this value is substituted in equation (34) or (34a), we get the weight of the air discharged from

$$G = G_1 \left( \frac{p_1 - p}{p_1} \right), \quad \dots \dots \dots (34a)$$

and the volume (measured at the pressure  $p_1$ ) from

$$V = V_1 \left( \frac{p_1 - p}{p_1} \right) \dots \dots \dots (34c)$$

These latter equations give rise to some important remarks. First of all we recognize that with the help of equation (37) the

value of  $\kappa$  can be found, provided we determine the three pressures  $p_1$ ,  $p_x$ , and  $p$  at the beginning and the end of the efflux, and at the equalization of temperature, and from equation (37) we then get the important magnitude  $\kappa$ ,

$$\kappa = \frac{\log p_1 - \log p_x}{\log p_1 - \log p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37a)$$

In this way experiments were made by Gay-Lussac and Welter, by Masson, Dupré, Cazin, Hirn, Weisbach, and Röntgen; but although the experiments seem so simple, they differ considerably from each other and in such a way that the quantity  $\kappa$  is in most cases considerably smaller than 1.410. The experiments of Cazin,<sup>1</sup> Weisbach,<sup>2</sup> and Röntgen<sup>3</sup> appear to be the most reliable.

Weisbach made his observations under particularly favorable circumstances for his discharging vessel (an ordinary cylindrical steam-boiler) had the very considerable cubic contents of  $V_1 = 4.6720$  cbm. [165 cu. ft.]; the orifice of efflux had the diameter of 40 mm. [1.575 in.] and was open only a few seconds.

In one of his time experiments, measured in millimeters of mercury [in. of mercury], the three observed pressures were:

$$\begin{aligned} p_1 &= 1452.2, & p_x &= 1323.2, & p &= 1358.2 \\ [p_1 &= 57.174, & p_x &= 52.094, & p &= 53.473], \end{aligned}$$

and in the other experiment

$$\begin{aligned} p_1 &= 625.0, & p_x &= 494.0, & p &= 530.0 \\ [p_1 &= 24.606, & p_x &= 19.449, & p &= 20.866]. \end{aligned}$$

The first values gave, according to equation (37a),  $\kappa = 1.405$ , the other  $\kappa = 1.400$ , both of them somewhat smaller than 1.410.

The experiments of Röntgen were conducted with special care; from ten experiments with air he found an average value of  $\kappa = 1.4053$ ; from eight experiments with hydrogen  $\kappa = 1.3852$ , and

<sup>1</sup> Cazin, *Annales de Chimie et de Phys.* 3d Series, Vol. 66, p. 206.

<sup>2</sup> Weisbach, *Civilingenieur.* Vol. 5, 1859, p. 46.

<sup>3</sup> Röntgen, *Poggendorff's Annalen*, Vol. 148 (1873), p. 580.

from ten experiments with carbonic acid  $\kappa=1.3052$ . Instead of employing, like *Weisbach*, a mercury manometer, he used a very sensitive metal manometer; this vessel, however, had only the cubic contents  $V_1=0.070$  cbm. [2.472 cu. ft.]. The result, that these experiments make  $\kappa$  smaller than was to be expected, has always been ascribed to the fact that the assumptions were not fulfilled under which formulas (37), (37a) were developed; for even during the shortest period of efflux the walls of the vessel give off heat to the air within, whose temperature sinks comparatively quickly, and consequently  $p_x$  must become too large and  $\kappa$  too small. Accordingly it is to be expected that that experiment will give the most reliable results in which the orifice is open only a fraction of a second, and in which there is a very large orifice of efflux in order to obtain large pressure differences  $p_1-p_x$  and  $p-p_x$ , and thus secure accurate readings; but just these conditions are fulfilled in the experiments of *Hirn*,<sup>1</sup> and yet he found, as the mean of a large number of experiments with atmospheric air,  $\kappa=1.3845$ ; unfortunately he did not give the several observation values; to be sure, *Hirn* did not observe in his experiments the pressure  $p_x$  at the instant of closing the orifice, but assumed in his computation as self-evident that the pressure  $p_x$ , in the discharging vessel, in each of his experiments, fell to the external atmospheric pressure; the capacity of the discharging vessel with which *Hirn* experimented, moreover, only amounted to  $V_1=0.010$  cbm. [0.353 cu. ft.].

As was mentioned above, the deviations of the experimental results from the expected ones is ascribed to the circumstance that even in the shortest period of efflux the walls of the vessel gave off heat to the cooling gas. But the deviations may be due, and perhaps in a larger measure, to another circumstance. In deriving equation (37) it has always been assumed that, from the beginning to the end of efflux, a quantity of air remaining behind in the vessel expands not only adiabatically, but also in reversible fashion, and consequently expands, overcoming the

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<sup>1</sup> *Hirn*, "Exposition de la théorie mécanique de la chaleur." Paris, 1875. 3d edition, Vol. I, p. 111.

full pressure of equilibrium; moreover it is assumed that the weight of the air flowing toward the orifice in a funnel-shaped space can be regarded as insignificant in comparison with the rest of the air existing in the vessel, an assumption which is evidently the less permissible the greater the orifice and the smaller the discharging vessel.

We must therefore assume that the expansion of the air takes place in *n o n - r e v e r s i b l e* fashion, accompanied by a stormy motion of all the air in the discharging vessel; this stormy motion appears to promote a far more rapid exchange of heat between the walls of the vessel and the air. The rapid exchange of heat, which can be inferred from the experiments, appears to be difficult to understand, if we only think of the quiet reversible expansion, because, as is well known, in such poor heat conductors as gases, heat can only be transmitted very slowly in a state of rest.

From all this it can be concluded that the foregoing experimental method, for the determination of the value  $\kappa$ , is in *p r i n c i p l e u n r e l i a b l e*, because the assumptions are not fulfilled which were employed in deriving equation (37). The *W e i s b a c h* experiments correspond more closely to these assumptions, because in them there was a large discharging vessel. If these objections are sound and if the expansion is non-reversible, then, after closing the orifice, a rise of pressure should be observed, even when there is no heat imparted by the walls of the vessel to the air. The passage of the stormy motion into a condition of equilibrium, which is manifested by the increase of pressure, undoubtedly takes place with extraordinary rapidity, and consequently immediately after the closing of the orifice there is an almost jump-like rise of pressure. This jump I have in fact observed when I repeated the *W e i s b a c h* experiments in the modified form, which, like my own, were instituted for other purposes, namely, for the investigation of the efflux of air from the orifices of vessels. The discharging vessel (an iron boiler with which I made the experiments) had a capacity of  $V_1 = 0.81088$  cbm. [28.637 cu. ft.] (determined by a careful calibration with water); the pressure of the air in the interior was observed by an open mercury manometer. The ratio of the cross-section of



the vessel and the cross-section of the manometer tube was exactly 200.

Now when the vessel is filled with compressed air and, after equalization of temperature, the orifice of efflux opened and then closed again after a short period, there occur the pressure variations represented schematically in Fig. 28. The abscissa  $OA$

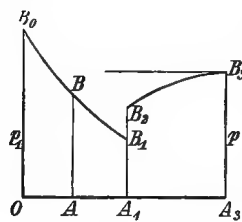


FIG. 28.

represents the time which has elapsed from the opening of the orifice, and the ordinate  $AB$  represents the pressure of the air, measured by the mercury column, for the assumed instant of time; at the beginning of the time, and therefore at the moment of opening the orifice, the pressure  $p_1$  is measured by  $OB_0$ ; at the instant of closing the orifice (at the time  $OA_1$ , which in all my experiments on the average amounted to 10 seconds) a high pressure  $p_x$  is observed, and, as represented by the ordinate  $A_1B_1$ , this pressure can be read from the manometer with sufficient certainty; now here the observed phenomenon occurs, namely, that the pressure  $p_x$  jumps suddenly to the larger value  $p_y$  (from  $A_1B_1$  to  $A_1B_2$ ), remains stationary for a moment, and gradually increases, somewhat like the course of the curve  $B_2B_3$ , at first rapidly and then more slowly, till finally, after a sufficiently long time ( $OA_3$ ), it remains stationary at the value  $p = A_3B_3$ ; the course of the pressures in the latter period corresponds to the gradual equalization of temperature. The observation of the pressure  $p_y$  is tainted with the same uncertainty, but the jump  $p_y - p_x$  in the following experiments amounted to 13 mm. [5.2 in.] of mercury column; the jump was greater the higher the initial pressure in the boiler; for initial pressures less than two atmospheres the jump phenomenon disappeared; Weisbach's experiments did not exceed this initial pressure, but a much less excess of pressure existed in the experiments of some of the other experimenters, which perhaps explains why none of them mentioned the phenomenon. Only de Saint-Venant and Wantzel have observed a similar phenomenon in their experiments, discussed above, and say expressly that the top of the mercury column

in the manometer made a jumping motion of about 1 to 3 mm. [0.4 to .12 in.] at the instant of closing the orifice.

One is inclined to ascribe the phenomena exclusively to the inertia of the mercury column in the manometer tube; during the efflux the surface of the mercury sinks in accelerated fashion, and the constantly diminishing mercury column assumes a certain velocity so that its surface outruns its true position when the orifice closes and its immediate return to an instantaneous position of equilibrium seems explicable.

But closer reflection shows that this procedure is not sufficient to explain the phenomenon; we should rather seek in it the proof that in reality the quantity of air remaining behind does not expand in reversible fashion during the efflux, and that the rapid rise of pressure is, in the main, to be ascribed to the passage of the stormy motion into a condition of equilibrium.

From the great number <sup>1</sup> of my different observations, one will be picked out as an example.

**Example.** In one experiment the pressures, measured in millimeters [inches] of mercury, were as follows: The initial pressure  $p_1 = 2809.5$  [110.61], the pressure  $p_x$  at the instant of closing the orifice was equal to 2584.9 [101.77], at the end of the jump  $p_y = 2597.4$  [102.24], and after equal-

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<sup>1</sup> A short account of these experiments with the description of the experimental apparatus and method can be found in *Der Civilingenieur*, 1874, Vol. 20, p. 1: "Resultate experimenteller Untersuchungen über das Ausströmen der Luft bei starkem Überdruck."

The experiments of 1871 were conducted by me in Zurich with the apparatus which belonged to the machinery collection of the Confederation's Polytechnikum, and which was constructed according to my directions. As I left Zurich a few months after the completion of the apparatus, I had to limit the experiments to the investigation of a question which will be discussed later in the text. The question touched upon above I could unfortunately not pursue more thoroughly in an experimental way.

It would be of great value if the experiments with high pressure could be taken up again by others; the highest pressure in *Weisbach's* experiments only went to 2 atmospheres, in my experiments it went to 4 atmospheres. The greatest difficulties are encountered by virtue of the fact that at high pressures the air penetrates the metallic pores; in my apparatus the air went through the inch walls of the metal dome. After much trying, and after the inner walls of the boiler were painted with red lead and all brass domes (mountings) were dipped into boiling linseed oil, we succeeded in making the apparatus air-tight and in avoiding losses of air.

ization of temperature  $p = 2639.9$  [103.93]; the temperature of the external air was  $t_1 = 14.6^\circ \text{ C.}$  [ $58.28^\circ \text{ F.}$ ]; the barometer reading was 722.1 mm. [28.43 in.], the air flowed for 9.9 seconds through a circular, well-rounded, orifice having a diameter of 5.73 mm. [0.2256 in.]. Boiler capacity  $V_1 = 0.81088 \text{ cbm.}$  [28.637 cu. ft.]. Here we first compute the weight of air which the boiler contained at the beginning and at the end of the experiment according to the formulas

$$V_1 p_1 = G_1 B T_1 \quad \text{and} \quad V_1 p = G_x B T_1,$$

where  $B = 29.269$  [53.349]; for the pressures we must substitute the specific values obtained by multiplying the pressure in millimeters of mercury by 10333:760 [2116.31:29.922]. In the present case there results:

$$G_1 = 3.6796 \quad \text{and} \quad G_x = 3.4575 \text{ kg.} \\ [G_1 = 8.1124 \quad \text{and} \quad G_x = 7.6227 \text{ lb.}]$$

The difference  $G_1 - G_x$  is the quantity of air discharged in 9.9 seconds; these values are moreover independent of all occurrences which happen at the close of the orifice. According to equation (24), p. 180, if we replace the exponent by the letter  $r$ , and thus assume that the quantity of air  $G_x$  remaining behind expands during the period of efflux according to the law  $p v^r = \text{constant}$ , we can compute, with the help of the preceding experimental data,

$$r = 1.338,$$

which is essentially smaller than  $\kappa = 1.410$ .

The work  $L$ , which the air remaining behind performed on the discharged air, is, according to equation (7b), p. 154,

$$L = \frac{1}{r-1} (V' p_1 - V_1 p_x),$$

when its initial volume at the pressure  $p_1$  is designated by  $V'$ .

Now if  $p_v$  really corresponds to the equilibrium pressure, the change of inner work of the air remaining behind, according to equation (52), p. 132, is

$$U - U_1 = \frac{1}{\kappa - 1} (V_1 p_v - V' p_1),$$

and then the quantity of heat  $Q$ , which the air remaining behind absorbs from the walls of the vessel during the period of efflux, can be computed from the formula

$$Q = A(U - U_1 + L),$$

where the volume  $V'$  of the preceding equations can be determined from

$$V' = V_1 \left( \frac{p_x}{p_1} \right)^{\frac{1}{r}}.$$

The calculation can easily be pursued further even for this present example. However we will simply remark that the quantity of heat and the work just computed relate only to the air remaining behind. But the quantity of air discharged has likewise absorbed heat and done work on the air preceding it. A further discussion of the problem would lead us too far for the purpose of the present book.

### § 38. FLOW OF A GAS FROM ONE VESSEL INTO ANOTHER WITH VARIABLE VESSEL-VOLUME AND WHEN HEAT IS IMPARTED.

In the general case, which was made the basis of the investigations of the last article, the flow of the gas from one space to another, the capacity of both vessels was regarded as constant (§ 35, p. 178, Fig. 27), and at the same time the limiting assumption was made that no heat was imparted to either one vessel or the other during the efflux. If we drop the limitations mentioned, then we strike the problem which is of technical importance, because it arises in the fuller investigation of air engines.<sup>1</sup>

For the clarification of the problem, suppose the three pistons  $K_1$ ,  $K$ , and  $K_2$  (Fig. 29) to form with the cylinder the spaces  $A$  and  $B$  which are filled with air. Let the middle piston  $K$  (called the transfer-piston in air engines) be regarded as impenetrable to heat, and let it contain perforations which are provided with valves. In a part of these holes the valves open in one direction, and in the other part in the opposite direction, so that all changes of pressure occurring in the two spaces are immediately equalized by the flow of a corresponding quantity of air, through the answering valve, out of one space into the other; then the pressure  $p$ , in itself variable, nevertheless always possesses the same value in the two spaces.

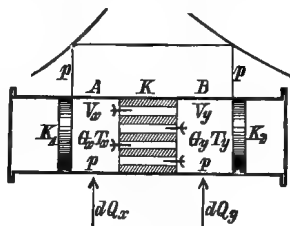


FIG. 29.

<sup>1</sup> The problem was first treated by the author in *Der Civilingenieur*, 1883, Vol. 29, p. 557: "Über die Wirkung des Verdrängers bei Heiss- und Kaltluftmaschinen."

Let the space  $A$  have the variable volume  $V_x$  and, at the moment in question, let it enclose  $G_x$  kg. [lb.] of air of the temperature  $T_x$ ; in the other space  $B$  let there be at the same time the volume  $V_y$ , containing  $G_y$  kg. [lb.] of air of the temperature  $T_y$ , but, for the reasons mentioned, possessing the same pressure  $p$  as the space  $A$ .

Now if we suppose the piston  $K$  to be stationary and, in any way whatever, heat to be supplied to, or withdrawn from, the two spaces  $A$  and  $B$ , the two pistons  $K_1$  and  $K_2$  simultaneously retreating and performing work, then the problem arises of the state of the air in the one space, and in the other space for any piston position whatever; the question also is as to the quantities of work which have been produced or consumed, and finally as to the quantity of heat which has been absorbed or rejected by the one space and the other space.

It is worthy of note that the same law of change of the spaces  $V_x$  and  $V_y$  can be brought about if we regard one of the two external pistons  $K_1$  and  $K_2$  (Fig. 29) as stationary and the other two pistons movable, which cases in fact occur in constructed air engines; the valves mentioned as closing the holes in the transfer piston do not exist in the actual constructions, but have been assumed here for the purpose of more easily following the theoretical developments.

Let us first assume the valves in the holes to be closed, then the equation of condition of gases gives for the air in space  $A$  the relation

$$V_x p = B G_x T_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

and for the space  $B$

$$V_y p = B G_y T_y. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Let  $V$  designate the variable total volume, and let  $G$  be the total constant weight of the air in the two spaces, then we have

$$V = V_x + V_y$$

and

$$G = G_x + G_y;$$

from the addition of equations (38) and (39) follows

$$Vp = B(G_x T_x + G_y T_y). \quad . \quad . \quad . \quad . \quad . \quad (40)$$

If under like circumstances the temperature in the two spaces is equally great and equal to  $T$ , the relation  $Vp = BGT$  holds, and the foregoing equation then becomes

$$GT = G_x T_x + G_y T_y, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

from which formula the mean temperature  $T$ , i.e., the equalized temperature, can be computed; the introduction of this magnitude renders some of the following investigations easier.

The combination of equation (38) and equation (39) moreover gives

$$\frac{BG}{p} = \frac{V_x}{T_x} + \frac{V_y}{T_y}, \quad . \quad . \quad . \quad . \quad . \quad (42)$$

because  $G = G_x + G_y$ , or, using the relation  $Vp = BGT$ ,

$$\frac{V}{T} = \frac{V_x}{T_x} + \frac{V_y}{T_y}. \quad . \quad . \quad . \quad . \quad . \quad (42a)$$

Now supply to the closed space  $A$  the quantity of heat  $dQ_x$  and to the space  $B$  the heat  $dQ_y$ , and in so doing let the volume  $V_x$  increase by  $dV_x$  and  $V_y$  by  $dV_y$ , and let the corresponding change of pressure be  $dp'$  in space  $A$  and  $dp''$  in space  $B$ , and let the corresponding changes of temperature be designated by  $dT_x'$  and  $dT_y'$ ; then we can here use equations (12c) and (12e), p. 171, and obtain

$$dQ_x = \frac{A}{\kappa - 1} (V_x dp' + p dV_x) \quad . \quad . \quad . \quad . \quad (43a)$$

$$= c_p G_x \left( dT_x' - \frac{\kappa - 1}{\kappa} T_x \frac{dp'}{p} \right) \quad . \quad . \quad . \quad (43b)$$

and

$$dQ_y = \frac{A}{\kappa - 1} (V_y dp'' + \kappa p dV_y) \quad . \quad . \quad . \quad . \quad (44a)$$

$$= c_p G_y \left( dT_y' - \frac{\kappa - 1}{\kappa} T_y \frac{dp''}{p} \right). \quad . \quad . \quad . \quad (44b)$$

After the two separate spaces have been supplied with the given quantities of heat imagine the valves in the passages (Fig. 29) to be opened until equalization of pressure has taken place; then, at the end, the pressure in both spaces will be  $p+dp$ . Furthermore, after equalization of pressure, let  $T_x+dT_x$  be the temperature in the space  $A$ , and  $T_y+dT_y$  that in the space  $B$ .

The introduced differentials can now be easily determined; first of all, as regards the relation between  $dp'$ ,  $dp''$ , and  $dp$  we have in equation (20a), p. 176, when applied to the present case, simply to substitute  $p+dp$  in place of  $p$ ,  $p+dp'$  in place of  $p_1$ , and  $p+dp''$  in place of  $p_2$ ; also  $V_x+dV_x$  in place of  $V_1$ , and  $V_y+dV_y$  in place of  $V_2$ ; we then get

$$p+dp = \frac{(V_x+dV_x)(p+dp') + (V_y+dV_y)(p+dp'')}{V_x+dV_x + V_y+dV_y}.$$

Hence there follows, when the multiplication is effected and differentials of higher order are neglected in comparison with those of the lower order,

$$dp = \frac{V_x dp' + V_y dp''}{V_x + V_y},$$

and because the denominator of this fraction simply represents the instantaneous total volume  $V$  we get

$$V dp = V_x dp' + V_y dp''. \quad . \quad . \quad . \quad . \quad . \quad (45)$$

We get besides, from differentiation of  $V = V_x + V_y$ ,

$$dV = dV_x + dV_y. \quad . \quad . \quad . \quad . \quad . \quad (45a)$$

Now if we add the two equations (43a) and (44a) we get in the value  $dQ_x + dQ_y$ , which we will designate by  $dQ$ , the whole quantity of heat absorbed by the air in the two spaces  $A$  and  $B$ , or

$$dQ = \frac{A}{\kappa - 1} [V_x dp' + V_y dp'' + \kappa p (dV_x + dV_y)];$$

or, utilizing equations (45) and (45a),

$$dQ = \frac{A}{\kappa - 1} (V dp + \kappa p dV). \quad . \quad . \quad . \quad . \quad . \quad (46)$$

This equation gives for the present investigations an interesting and important result. The equation is identical with equation (12c), p. 171, and enunciates that the quantity of heat  $dQ$ , which has been absorbed by the whole quantity of air in both spaces and partly transformed into work, is determined exactly as if the air existed in only one space,  $V$ , under the pressure  $p$ . The same law also holds with respect to the external work produced; the work in the space  $A$  is  $pdV_x$ , and in the other space  $pdV_y$ ; the whole external work is therefore

$$dL = p(dV_x + dV_y) = pdV,$$

and as if the air filled only one space  $V$ .

We recognize, moreover, that the present propositions are valid for more than two spaces; no matter how the weight  $G$  of the air may be distributed in the several spaces, no matter what temperature may exist in each of the several spaces, the quantity of heat developed by the total mass of the air and the quantity of work which it produced or consumed can be always computed by equation (46), as if the air occupied only one space, provided the spaces are so connected with each other that in all of them the same pressure  $p$  prevails.

Equation (46) can easily be brought into the other forms given under (12), p. 171, if we introduce for  $T$  the mean or equalization temperature.

We will present only one of these transformations. From the already used relation

$$Vp = BGT$$

there follows, by differentiation,

$$Vdp + pdV = BGdT,$$

and if we divide this expression by the preceding we get

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T}.$$

Equation (46) can also be written as follows:

$$dQ = \frac{AVp}{\kappa - 1} \left[ \frac{dp}{p} + \kappa \frac{dV}{V} \right],$$



and from this results, if we eliminate  $\frac{dV}{V}$  from the last two equations and use the relation (54), p. 134,

$$dQ = c_p G \left[ dT - \frac{\kappa - 1}{\kappa} T \frac{dp}{p} \right]. \quad . \quad . \quad . \quad . \quad (46a)$$

Consequently what was said of equation (46) is true of this formula, only we have to remember in using it that  $T$  is the mean temperature determined according to equation (41).

Finally as regards the main purpose of the problem, namely, the determination of the quantities of heat  $Q_x$  and  $Q_y$ , which can be separately imparted to each of the two spaces, we must first know which is the discharging and which the receiving space during the equalization of pressure; if we assume in the following that the air flows from  $A$  to  $B$ , then during the equalization of pressure the quantity of air which originally amounted to  $G_x$  kg. [lb.] will at the end amount to  $G_x - dG_x$ ; this quantity of air remaining behind expands adiabatically, consequently for this procedure the equations (24) and (25), p. 180, are valid; then we must put

$$\begin{array}{ll} p + dp \text{ in place of } p_x & \text{and } p + dp' \text{ in place of } p_1, \\ T_x + dT_x \text{ in place of } T_x & \text{and } T_x + dT_x' \text{ in place of } T_1, \\ G_x - dG_x \text{ in place of } G_x & \text{and } G_x \text{ in place of } G_1, \end{array}$$

and therefore get

$$\frac{p + dp}{p + dp'} = \left( \frac{G_x - dG_x}{G_x} \right)^\kappa$$

and

$$\frac{T_x + dT_x}{T_x + dT_x'} = \left( \frac{G_x - dG_x}{G_x} \right)^{\kappa - 1}.$$

If we multiply the left side of the formula above and below by  $(p - dp')$  and similarly the other by  $(T_x - dT_x')$ , and develop the expressions to the right according to the binomial theorem, and cancel the differentials of higher order and of the higher powers, we get the following relations:

$$dp' = dp + \kappa p \frac{dG_x}{G}$$

and

$$dT_x' = dT_x + (\kappa - 1)T_x \frac{dG_x}{G_x}.$$

With the help of equations (45) and (42) we could express in a similar manner the differentials  $dp''$  and  $dT_y'$ .

Now if we substitute the preceding values of  $dp'$  and  $dT_x'$  in equation (43b) there results

$$dQ_x = c_p G_x \left( dT_x - \frac{\kappa - 1}{\kappa} T_x \frac{dp}{p} \right), \quad . \quad . \quad . \quad (47)$$

or considering equation (38), p. 198, and equation (43), p. 124,

$$dQ_x = AV_x p \left[ \frac{\kappa}{\kappa - 1} \frac{dT_x}{T_x} - \frac{dp}{p} \right], \quad . \quad . \quad . \quad (47a)$$

and this formula likewise gives an interesting result which greatly facilitates the investigation of special cases; it enunciates that the quantity of heat  $dQ_x$  is determined as if the discharging space were shut-off, and the quantity of air  $G_x$  there existing were constant, while the temperature rise  $dT_x$  and the pressure rise  $dp$  need to proceed only so far as to correspond to the condition *after* the equalization of pressure.

The determination of the other quantity of heat  $dQ_y$ , which is to be supplied to the receiving space, now easily follows from the relation

$$dQ = dQ_x + dQ_y;$$

we find, when we use equations (46a) and (47),

$$dQ_y = c_p \left[ GdT - G_x dT_x - \frac{\kappa - 1}{\kappa} (GT - G_x T_x) \frac{dp}{p} \right],$$

or if we remember that because  $G = G_x + G_y$  we have  $dG_x = -dG_y$ , and if in addition we employ the relation which comes from equation (41), we get

$$dQ_y = c_p G_y \left[ dT_y - \frac{\kappa - 1}{\kappa} T_y \frac{dp}{p} \right] + c_p (T_y - T_x) dG_y, \quad . \quad . \quad (48)$$

or considering equation (39), p. 198, and equation (43), p. 124,

$$dQ_y = A V_y p \left[ \frac{\kappa}{\kappa - 1} \frac{dT_y}{T_y} - \frac{dp}{p} \right] + c_p (T_y - T_x) dG_y. \quad (48a)$$

The first term of the right-hand side again gives the quantity of heat to be supplied to the shut-off receiving space if the temperature and pressure are to be brought directly to the equalization values; but the second term corresponds to the quantity of heat which can be supplied to the transferred quantity of air  $dG_y$ , in order to heat it at the constant pressure  $p$  from  $T_x$  to  $T_y$ .

Inversely, if the space  $B$  is the discharging space and  $A$  the receiving space, the second term of equation (48) will disappear, and should be added to the right-hand side of equation (47) in the form  $c_p (T_x - T_y) dG$ . In most of the cases of the practical utilization of the preceding propositions it is guessed beforehand which of the two spaces  $A$  and  $B$  is the discharging- and which the receiving-space. In a doubtful case a guide is secured by the following consideration. Division of the two equations (38) and (39) gives

$$G_y = G_x \frac{V_y T_x}{V_x T_y};$$

consequently there follows, because the total weight of air in the two spaces  $G = G_x + G_y$  is constant,

$$G_x = \frac{G}{1 + \frac{V_y T_x}{V_x T_y}}.$$

Now if  $A$  is the discharging space, the denominator on the right-hand side of this expression must increase, and therefore the condition

$$d\left(\frac{V_y T_x}{V_x T_y}\right) > 0$$

must be satisfied.

The foregoing investigations form the basis for the solution of numerous problems of technical importance, but before discussing some of the most important we will give the graphical treatment

of a part of the problems, and thus extraordinarily facilitate an insight into the following problems and into the occurrences which exist in hot-air and cold-air engines.

In Fig. 30 suppose a cylinder, closed at one end, to have two movable pistons  $K$  and  $K_1$ , of which the first is the transfer-piston and is represented by a broken straight line. Let both pistons be supposed to be in motion and that the former at the beginning stands at  $K'$  and the other at  $K_1'$ ; the space to the left of the transfer-piston, at the time  $t$ , is designated by  $V_x$ , at the beginning by  $V_1$ ; at the time  $t$  let the space between the transfer piston and the outer piston, which latter we will call the power-piston, be designated by

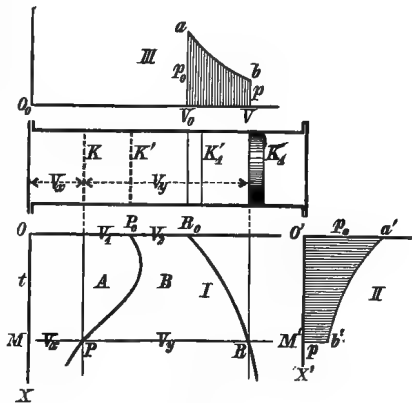


FIG. 30.

$v_y$  and at the beginning of the time (say  $t=0$ ) by  $V_2$ . We recognize moreover that the difference from the arrangement in Fig. 29 consists in that here one of the outer pistons  $K_1$  and  $K_2$  is left out, and as a compensation the transfer-piston is here movable, while there it was regarded as stationary; it amounts to the same thing in both cases, the arrangement in Fig. 29 is simply better suited for the development of the fundamental equations, while Fig. 30 is better suited for the explanation of the special investigations. In order to represent to the eye the law of change of the two spaces  $V_x$  and  $V_y$ , and hence the law of the piston motion, lay off  $OM$  in Fig. 30 from  $O$  downward on the axis of  $OX$  for the elapsed time  $t$ , and draw through  $M$  a horizontal on which the distance  $MP$  is to represent the volume  $V_x$  and the distance  $PR$  the volume  $V_y$ ; the whole distance  $MR$  then represents the total volume  $V = V_x + V_y$  of the air in the two spaces. At the beginning of the time ( $t=0$ ),  $OP_0$  similarly represents the volume  $V_1$ , and  $P_0R_0$  the volume  $V_2$ ; the sum of the two spaces  $V_1 + V_2$  is designated by  $V_0$  and is given by the distance  $OR_0$ .

From all this we see that when we think of continuous motion of both pistons the curves  $P_0R$  and  $R_0R$  present to the eye the law according to which  $V_x$ ,  $V_y$ , and  $V$  change with the time. I call this part of Fig. 30 designated by I the "piston diagram"<sup>1</sup>; to each piston there corresponds a particular value of the pressure  $p$  of the air in the two spaces; if we again lay off the elapsed time  $t$ , as  $O'M'$  from  $O'$  along the vertical axis  $O'X'$ , and make the horizontal distance  $M'b'$  equal to  $p$ , and make, for the beginning of the time ( $t=0$ ), the distance  $O'a'$  equal to the initial pressure  $p_0$ , we will get, in the curve  $a'b'$ , the law according to which the pressure in the whole interior of the cylinder varies with the time; we designate the corresponding part II of Fig. 30 as the "piston force diagram." Finally in the upper part of the figure, designated by III, there is drawn the ordinary "pressure- or indicator-diagram"; the curve  $ab$  (pressure curve) gives the variation of pressure which occurs when the total volume changes from  $V_0$  to  $V$ ; the area enclosed by the curve  $ab$  gives the work which is performed during expansion.

If, starting from a fixed point, we at one time lay off on a horizontal axis the variable volume  $MP=V_x$  as abscissa, and at another time the volume  $PR=V_y$ , and both times lay off the pressure  $p$  as ordinate, we shall get two more representations of the pressure curve, which have a practical significance for certain air engines because they can be obtained by the application of two indicators.

In engines the pistons are as a rule moved by cranks which turn with nearly uniform rotation; in this case the time interval  $OM$  is proportional to the crank angle, and the curves in the piston diagram are sinusoids, provided we assume infinitely long

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<sup>1</sup> The diagram presented, which I already gave in the second edition of this book (1866, p. 200), has since been widely used, and from that time I have utilized this method of representation in my lectures on steam engines, and particularly for the graphical computation of engines with several cylinders, the compound engines. A full illustration of it, with practical examples, is given by Schröter in the Zeitschrift des Vereins deutscher Ingenieure. 1884, Vol. 28, p. 191; he gave it, to be sure, without the addition of the piston force diagram, which latter renders good service in determining the turning force diagram and the degree of fluctuation in the motor of the engine.

connecting-rods, or curves resembling the sinusoids, if this condition is not fulfilled. In engines moreover the two pistons return periodically after each revolution to the initial positions, and the curve  $ab$  in diagram III (Fig. 30) then forms a closed curve; the whole process is transformed into a cycle which for certain engines will be subjected later on to a closer examination.

### § 39. APPLICATIONS AND SPECIAL PROBLEMS.

After the foregoing preliminaries we will now adduce a few examples which contain applications of the propositions given in § 38.

**Problem 1.** The power-piston  $K_1$  (Fig. 30) is held fast, on the other hand the transfer-piston  $K$  is shifted from right to left, so that space  $A$  experiences a decrease and space  $B$  an increase. Fig. 31 represents the corresponding diagram; since the total volume  $V = V_x + V_y = V_0$  is to be constant, the curve  $R_0R$  for the power-piston is a straight line parallel to the axis  $OX$ ; the curve  $P_0P$  gives the law according to which the shifting of the transfer-piston takes place with respect to the time,  $OP_0$  gives the initial volume  $V_1$  of the one space, and  $P_0R_0$  the initial volume  $V_2$  of second space; let  $T_1$  here be the temperature to the left of the transfer-piston and  $T_2$  that

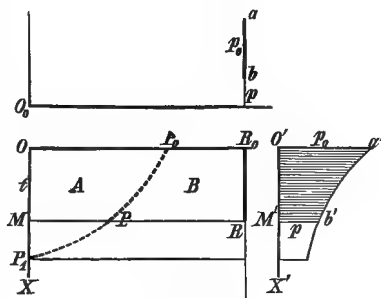


FIG. 31.

to the right,  $p_0$  the initial pressure in both spaces. After the time  $t$  the position of the transfer-piston is at  $P$ , and now there should be calculated, as unknown quantities, some of the magnitudes  $T_x$ ,  $T_y$ ,  $p$ ,  $Q_x$ , and  $Q_y$  corresponding to the values  $V_x$  and  $V_y = V_0 - V_x$ . The problem presents many special cases of which a few will be treated. First of all there is no doubt that, under the assumptions made, the space  $A$  to the left of the transfer-piston is a discharging space and  $B$  a receiving

space, and that external work is neither produced nor consumed because it is assumed that the total volume  $V$  is constantly equal to  $V_0$ .

*Special case a.* During the motion of the transfer-piston heat is neither imparted to, nor withdrawn from, the space  $A$  or the space  $B$ .

Therefore  $dQ_x=0$  and  $dQ_y=0$ , and consequently also  $dQ=0$ . Because also  $dV=0$  it follows from equations (46) and (46a) that  $dp=0$  and  $dT=0$ ; we therefore obtain the result that during shifting of the transfer-piston the pressure  $p$  and the mean temperature  $T$  remain unchanged in the two spaces, remain respectively at  $p_0$  and  $T_0$ . Of course in so doing (as it is now only a question of theoretical elucidation) we must imagine the transfer-piston to move slowly and must assume that the flow from one space into the other (through the transfer-piston) takes place without resistance.

The substitution of  $dp=0$  and of  $dQ_x=0$  in equation (47) gives also  $dT_x=0$ , from which is to be concluded that, during the whole occurrence, the temperature  $T_x$  remains constant and therefore  $T_x=T_1$ .

Matters are different in the receiving space  $B$ . Here the temperature  $T_y$  is variable and can be computed from equation (42a), making use of the preceding notation, as follows:

$$T_y = \frac{V_0 - V_x}{V_0} \cdot \frac{T_0}{T_1} \quad (49)$$

As  $p$  was found to be constant, we have in the present case for the pressure curve  $a'b'$  (Fig. 31) a straight line parallel to the axis  $O'X'$ .

Therefore, among all the quantities occurring in the calculation, it is solely the temperature  $T_y$  which varies with  $V_x$ .

If we should now bring the transfer-piston back to the original position, then, for the return motion, the space  $B$  would be the discharging space and  $A$  the receiving space, the temperature  $T_y$  would remain constant and the temperature  $T_1$  would assume another value; we see at once without further cal-

ulation that by the continual reciprocating motion of the transfer-piston a gradual equalization of temperature results till finally there exists in both spaces the mean temperature  $T_0$ .

If we shift the transfer-piston immediately from position  $P_0$  (Fig. 31) to the left end  $P_1$ , then  $V_x=0$ , all air is pushed into the space  $V_y$ , and equation (49) gives  $T_y=T_0$ ; the mean temperature is therefore immediately established, and further shifting of the transfer-piston will not cause any more changes in the pressure and temperature of the air in the two spaces.

*Special case b.* The temperature of the air is to remain constant in the two spaces, while the power-piston is held fast and the transfer-piston moves.

This assumption demands that heat be imparted and withdrawn, as the case may be, on both sides of the transfer-piston. Because here  $T_x=T_1$  and  $T_y=T_2$ , we have from equation (42)

$$\frac{BG}{p} = \frac{V_x}{T_1} + \frac{V_y}{T_2},$$

and, for the initial position of the transfer-piston,

$$\frac{BG}{p_0} = \frac{V_1}{T_1} + \frac{V_2}{T_2},$$

and hence, by division of the two equations,

$$\frac{p}{p_0} = \frac{V_1 T_2 + V_2 T_1}{V_x T_2 + V_y T_1} \cdot \cdot \cdot \cdot \cdot \quad (50)$$

If we designate the constant ratio  $T_2 : T_1$  by  $\lambda$  and put  $V_2 = V_0 - V_1$ , also  $V_y = V_0 - V_x$ , then from the foregoing formula we get

$$\frac{p}{p_0} = \frac{V_0 + (\lambda - 1)V_1}{V_0 + (\lambda - 1)V_x}; \cdot \cdot \cdot \cdot \cdot \quad (50a)$$

consequently the pressure  $p$  in both spaces changes with the shifting of the transfer-piston, and can be easily computed from every value of  $V_x$ . If the volume  $V_x$  diminishes, as is assumed in Fig. 31, an increase of pressure  $p$  occurs when  $\lambda > 1$  or  $T_2 > T_1$ ,



or when, as is said in discussing hot-air engines, air is forced from the cold space  $A$  to the hot space  $B$ . On the other hand if, for the same motion of the transfer-piston,  $A$  were the hot space and  $B$  the cold space so that  $T_2 < T_1$  and  $\lambda < 1$ , then, according to equation (50), the pressure  $p$  would diminish in both spaces.

From equation (46), and because  $V = V_0$  and  $dV = 0$ , we can now determine for the present case the total quantity of heat  $Q$  consumed in the two spaces,

$$Q = \frac{AV_0}{\kappa - 1}(p - p_0) \dots \dots \dots (51)$$

On the other hand, because  $T_x = T_1$  and  $dT_x = 0$ , equation (47) gives the quantity of heat  $dQ_x$  which must be supplied to the discharging space  $A$ , and, at the same time considering equation (38) and the relation  $AB = c_p \frac{(\kappa - 1)}{\kappa}$ , we get

$$dQ_x = -AV_x dp, \dots \dots \dots (52a)$$

and from this, by integration and the utilization of equation (50a),

$$G_x = \frac{A}{\lambda - 1} \left[ V_0(p - p_0) - [V_0 + (\lambda - 1)V_1]p_0 \log_e \frac{p}{p_0} \right] \dots (52)$$

Finally we get for the quantity of heat  $Q_y$ , which must be *supplied from without* to the receiving space  $B$ , with the help of the relation  $Q = Q_x + Q_y$  and the utilization of the foregoing expressions,

$$Q_y = \frac{A}{\lambda - 1} \left[ \frac{(\lambda - \kappa)}{(\kappa - 1)} V_0(p - p_0) + [V_0 + (\lambda - 1)V_1]p_0 \log_e \frac{p}{p_0} \right], \quad (53)$$

and we thus can answer all questions relating to the present special case.

If we assume as a special case that at the beginning the transfer-piston stands at the right end  $R_0$  of the cylinder, Fig. 31, and is pushed to the left end  $P_1$ , so that the total quantity of air existing at the beginning in the space  $A$  is completely transferred to

the space  $B$ , then in the foregoing formulas we must substitute  $V_2=0$ ,  $V_1=V_0$ , and  $V_x=0$ ; we therefore get from equation (50a)

$$\frac{p}{p_0} = \lambda = \frac{T_2}{T_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50b)$$

and equations (51), (52), and (53) give, if we make  $p=\lambda p_0$ ,

$$Q = \frac{\lambda-1}{\kappa-1} A V_0 p_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51a)$$

$$Q_x = \left(1 - \frac{\lambda}{\lambda-1} \log_e \lambda\right) A V_0 p_0, \quad . \quad . \quad . \quad . \quad (52b)$$

$$Q_v = \left(\frac{\lambda-\kappa}{\kappa-1} + \frac{\lambda}{\lambda-1} \log_e \lambda\right) A V_0 p_0. \quad . \quad . \quad . \quad (53a)$$

Since, in accordance with the hypothesis, the total quantity of air of the weight  $G$  existed at the beginning in the space  $V_0$ , under the pressure  $p_0$  and with the temperature  $T_1$ , there is valid the relation  $V_0 p_0 = BGT_1$  or, considering equation (54), p. 134,  $AV_0 p_0 = c_v(\kappa-1)GT_1$ ; consequently from equation (51a) there follows

$$Q = c_v G (T_2 - T_1).$$

The quantity of heat which the total weight of gas has consumed or produced during the assumed procedure is therefore found to be exactly as much as if the transfer-piston were absent and the air simply brought under constant volume from the temperature  $T_1$  to the temperature  $T_2$ .

But if we ask what quantities of heat really are to be supplied and withdrawn when the change of temperature occurs under constant volume with the help of the transfer-piston, then equations (52a) and (52b) must be considered.

For example if  $\lambda=2$ , and therefore the temperature  $T_2$  in the receiving space  $B$  is double that of temperature  $T_1$  in the discharging space  $A$  (say according to Celsius  $t_1=25^\circ$  and  $t_2=323^\circ$ ) [ $t_1=77^\circ$  F. and  $t_2=613.4^\circ$  F.], then equation (51a) gives

$$Q = 2.4390 A V_0 p_0,$$

and equations (52b) and (53a) give

$$Q_x = -0.3862 AV_0 p_0 \quad \text{and} \quad Q_y = +2.8252 AV_0 p_0;$$

consequently heat must be withdrawn from the discharging space  $A$  and heat must be imparted to the receiving space  $B$ , and this latter quantity of heat  $Q_y$  is greater than the quantity of heat  $Q$  which must be imparted to the total quantity of air at constant volume for the same rise of temperature and when the quantity of air fills only one space and there is no transfer-piston. We already recognize in this simple case that, for the processes described by air engines working with transfer-pistons, heat supply and withdrawal must be computed according to different formulas from those hitherto employed in technical circles.

**Problem 2.** The transfer-piston  $K$  (Fig. 30, p. 205) is stationary and therefore  $V_x = V_1$  constant, while the power piston  $K_1$  moves and therefore the volume  $V_y$  as well as  $V = V_1 + V_y$  is variable. Here there is a production or a consumption of external work according as there is an increase or decrease of the volume  $V_y$ , and hence also of the volume  $V$ , according as one thinks of expansion or of compression.

The problem can embrace an unlimited number of special cases of which the technically important ones will be considered.

*Special case a.* Heat is neither imparted to, nor withdrawn from, space  $A$  or space  $B$ .

( $\alpha$ ) Expansion (Fig. 32).

Corresponding to the present problem,  $V_x$  is constant and therefore  $dV_x = 0$ ; furthermore  $dQ_x = 0$  and  $dQ_y = 0$ , it therefore follows that  $dQ = 0$ , and, because of the assumed expansion,  $A$  is the discharging space.

Here follow at once from equations (46) and (46a) the formulas

$$\frac{p}{p_0} = \left( \frac{V_0}{V} \right)^\kappa \quad . . . . . (54)$$

and

$$\frac{T}{T_0} = \left( \frac{p}{p_0} \right)^{\frac{\kappa-1}{\kappa}} = \left( \frac{V_0}{V} \right)^{\kappa-1}, \quad . . . . . (55)$$

where  $T_0$  is the mean temperature at the beginning; from these can be found the pressure  $p$  and the mean temperature  $T$  in both spaces for every value  $V$  of the total volume. We see that the curve  $ab$  of the pressure changes is the ordinary adiabatic, and

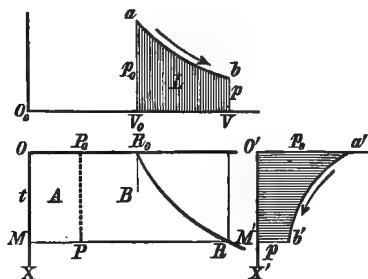


FIG. 32.

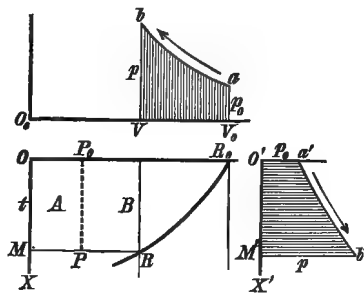


FIG. 33.

consequently the work  $L$  produced during expansion is found, equation (62b), p. 140, to be

$$L = \frac{1}{\kappa - 1} (V_0 p_0 - V p). \quad (56)$$

The change of temperature in the two spaces still remains to be determined. Because  $dQ_x = 0$ , equation (47) at once gives

$$\frac{T_x}{T_1} = \left( \frac{p}{p_0} \right)^{\frac{\kappa - 1}{\kappa}},$$

and by consideration of equation (55)

$$T_x = T_1 \left( \frac{V_0}{V} \right)^{\kappa - 1}, \quad (57)$$

while temperature  $T_y$  is determined from equation (42a) when there is substituted  $V_y = V - V_1$ ; we thus get

$$T_y = \frac{V - V_1}{\frac{V}{T} - \frac{V_1}{T_x}}, \quad (58)$$

in which formula all quantities in the right member are known.

( $\beta$ ) C o m p r e s s i o n (Fig. 33).

In the case of compression the space  $B$  is the discharging space. We see at once that equations (54) and (55) remain unchanged, and equation (56) likewise holds.

For the determination of the temperature values equation (48) holds because  $dQ=0$ , and in this equation the second term of the last member is omitted because the space in question is the discharging space; we get, with the help of equation (55),

$$\frac{T_y}{T_2} = \left(\frac{p}{p_0}\right)^{\frac{\kappa-1}{\kappa}} = \left(\frac{V_0}{V}\right)^{\kappa-1}, \quad . \quad . \quad . \quad . \quad (58a)$$

and we get  $T_x$  from equation (42a), if we there substitute  $V_x=V_1$  and  $V_y=V-V_1$ , namely,

$$T_x = \frac{V_1}{\frac{V}{T} - \frac{V_1}{T_y}}. \quad . \quad . \quad . \quad . \quad . \quad (57a)$$

For example, if the total quantity of air existing in the space  $B$  is to be forced into the space  $A$  possessing the volume  $V_1$ , then the final pressure there will be, according to equation (54), and because we must have  $V=V_1$ ,

$$p = p_0 \left(\frac{V_0}{V_1}\right)^{\kappa}. \quad . \quad . \quad . \quad . \quad . \quad (54a)$$

Furthermore the temperature there will be, according to equation (57a),  $T_x=T$  or, according to equation (55),

$$T_x = T_0 \left(\frac{V_0}{V_1}\right)^{\kappa-1}, \quad . \quad . \quad . \quad . \quad . \quad (57b)$$

where the mean temperature  $T_0$  at the beginning, according to equation (42a), must be computed from the following formula:

$$\frac{V_0}{T_0} = \frac{V_1}{T_1} + \frac{V_2}{T_2}.$$

The work  $L$  necessary for thus forcing the air is found from equation (56) to be

$$L = \frac{V_0 p_0}{\kappa - 1} \left[ \left( \frac{V_0}{V_1} \right)^{\kappa - 1} - 1 \right]. \quad (56a)$$

*Special case b.* The temperature in both spaces is kept constant, therefore  $T_x = T_1$  and  $T_y = T_2$ .

( $\alpha$ ) Expansion (Fig. 32).

Here equation (50) is at once valid, we have only to substitute  $V_x = V_1$ ; moreover if we designate the temperature ratio  $T_2 : T_1$  by  $\lambda$ , we get first

$$\frac{p}{p_0} = \frac{\lambda V_1 + V_2}{\lambda V_1 + V_y}, \quad (59)$$

whereby the course of the expansion curve  $ab$  is determined. Because  $dV = dY_y$  the outer work  $L$  performed is found by integrating between the limits  $V_2$  and  $V_y$ , and then

$$L = \int p dV = (\lambda V_1 + V_2) p_0 \log_e \frac{p_0}{p}. \quad (60)$$

The total quantity of heat  $Q$  needed by the air in the two spaces can be easily found from equation (46) to be

$$Q = \frac{\lambda - 1}{\kappa - 1} A V_1 (p_0 - p) + A (\lambda V_1 + V_2) p_0 \log_e \frac{p_0}{p}. \quad (61)$$

The quantity of heat  $Q_x$  which must be supplied to the here constant, discharging, space  $A$  can be found from equation (47), because  $T_x = T_1$ ,  $dT_x = 0$ , and  $B G_x T_x = V_1 p$ :

$$Q_x = A V_1 (p_0 - p), \quad (62)$$

and because of the relation  $Q = Q_x + Q_y$  the quantity of heat  $Q_y$ , which must be imparted to the receiving space  $B$ , is

$$Q_y = \frac{\lambda - \kappa}{\kappa - 1} A V_1 (p_0 - p) + A (\lambda V_1 + V_2) p_0 \log_e \frac{p_0}{p}. \quad (63)$$

These formulas hold for every value of  $\lambda$ , and it is consequently a matter of indifference in which space the temperature is the higher.

( $\beta$ ) C o m p r e s s i o n (Fig. 33, p. 213).

Here the space  $B$  is the discharging space and we see at once that for the present case formulas (59), (60), and (61) are valid; but it is not so for the expressions (62) and (63) found for  $Q_x$  and  $Q_y$ .

If we maintain the introduced mathematical notation, we must, for the case of compression, omit the term  $c_p(T_y - T_x)dG_y$  in equation (48) and add it to equation (47) in the form  $c_p(T_x - T_y)dG_x$ . Equation (48) therefore gives

$$dQ_y = c_p G_y \left( dT_y - \frac{\kappa - 1}{\kappa} T_y \frac{dp}{p} \right),$$

and hence follows, with the utilization of equation (39) and because  $dT_y = 0$ , the relation

$$dQ_p = -AV_y dp,$$

and consequently, with the help of equation (59), we get for the quantity of heat  $Q_y$  which is to be supplied to the space  $B$ ,

$$Q_y = \lambda AV_1(p - p_0) - A(\lambda V_1 + V_2)p_0 \log_e \frac{p}{p_0}. \quad . \quad . \quad (63a)$$

On the other hand, the quantity of heat which is to be supplied to the constant, discharging, space  $A$  is determined from

$$Q_x = Q - Q_y = \frac{1 - \lambda\kappa}{\kappa - 1} AV_1(p - p_0). \quad . \quad . \quad . \quad (62a)$$

We see that, with respect to the quantities of heat to be supplied and withdrawn, the case of compression is not simply an inversion of the case of expansion, although the pressure curve is the same.

If, in the case of compression, the air is to be completely forced

out of the space  $B$  into the space  $A$ , we must put  $V_y=0$  in equation (59) and then the final pressure  $p$  can be determined and its value substituted in the remaining equations.

*Special case c.* The transfer-piston is held fast and the temperature is kept constant in the constant space  $A$ ; on the other hand, heat is neither supplied to, nor withdrawn from, the space  $B$ .

( $\alpha$ ) Expansion (Fig. 32, p. 213).

In accordance with the hypothesis we here have  $V_x=V_1$ ,  $T_x=T_1$ , and  $dQ_y=0$ , and as a result of the last assumption also  $dQ_x=dQ$ .

Here follows from equation (47a)

$$dQ_x = -AV_1 dp. \quad . \quad . \quad . \quad . \quad . \quad (64)$$

The combination of this equation with equation (46) gives

$$\frac{A}{\kappa-1} (V dp + \kappa p dV) = -AV_1 dp,$$

and taking into account the relation  $V=V_1+V_y$  we find at once, by integration, the equation of the expansion curve  $ab$  to be

$$\frac{p}{p_0} = \left( \frac{\kappa V_1 + V_2}{\kappa V_1 + V_y} \right)^\kappa. \quad . \quad . \quad . \quad . \quad . \quad (65)$$

The work  $L$  which is performed is found, by integration of the equation  $dL=pdV_y$  and after utilization of the preceding equation (65), to be

$$L = \frac{(\kappa V_1 + V_2)p_0}{\kappa-1} \left[ 1 - \left( \frac{p}{p_0} \right)^{\frac{\kappa-1}{\kappa}} \right], \quad . \quad . \quad . \quad . \quad . \quad (66)$$

and the quantity of heat  $Q_x$ , which is here to be supplied to the discharging space  $A$ , follows from equation (64), and is

$$Q_x = AV_1(p_0 - p). \quad . \quad . \quad . \quad . \quad . \quad (67)$$



Finally there must be determined the variable temperature  $T_y$  in the receiving space  $B$ , provided that the initial temperature  $T_2$  there is known. Here equation (42) gives for the beginning and the end of the expansion respectively

$$\frac{BG}{p_0} = \frac{V_1}{T_1} + \frac{V_2}{T_2} \quad \text{and} \quad \frac{BG}{p} = \frac{V_1}{T_1} + \frac{V_y}{T_y},$$

from which, by division, follows

$$\frac{V_y}{T_y} + \frac{V_1}{T_1} = \left( \frac{V_2}{T_2} + \frac{V_1}{T_1} \right) \frac{p_0}{p}. \quad \dots \quad (68)$$

Consequently  $T_y$  can be computed from every value of  $V_y$  and for the corresponding value of  $p$ .

( $\beta$ ) C o m p r e s s i o n (Fig. 33, p. 213).

Here the circumstances are very different from those of expansion. As the space  $B$  is now converted into the discharging space, we must omit the second term of the right member in equation (48), p. 203, and from this follows

$$dQ_y = c_p G_y \left( dT - \frac{\kappa - 1}{\kappa} T_y \frac{dp}{p} \right).$$

and from this in turn results, because  $dQ_y = 0$ ,

$$\frac{T_y}{T_2} = \left( \frac{p}{p_0} \right)^{\frac{\kappa - 1}{\kappa}}. \quad \dots \quad (69)$$

Consequently the temperature  $T_y$  in the space  $B$  is determined for every value of the pressure  $p$ .

On the other hand, because  $A$  is now the receiving space, equation (47) can be written

$$dQ_x = c_p G_x \left( dT_x - \frac{\kappa - 1}{\kappa} T_x \frac{dp}{p} \right) + c_p (T_x - T_y) dG_x.$$

But  $T_x = T_1$  and  $dT_x = 0$ , and the equation of condition gives  $BG_x T_1 = V_1 p$  and  $BT_1 dG_x = V_1 dp$ ; consequently the equation for  $dQ_x$  reduces to the following:

$$dQ_x = \frac{AV_1 dp}{\kappa - 1} \left( 1 - \kappa \frac{T_y}{T_1} \right);$$

and if we here utilize equation (59), we get, by integration, the quantity of heat  $Q_x$  which can be supplied to the constant space  $A$ :

$$Q_x = \frac{AV_1}{\kappa - 1} \left\{ (p - p_0) - \frac{\kappa^2}{2\kappa - 1} \frac{T_2}{T_1} p_0 \left[ \left( \frac{p}{p_0} \right)^{\frac{2\kappa - 1}{\kappa}} - 1 \right] \right\} \quad (70)$$

As regards the course of the compression curve  $ab$  (Fig. 33), here also the relation (68) holds, and if, for the sake of simplicity, we represent the ratio  $T_2 : T_1$  of the initial temperatures by  $\lambda$  and utilize the temperature  $T_y$  according to equation (69), we get for the equation of the curve

$$V_y = \left[ (\lambda V_1 + V_2) \frac{p_0}{p} - \lambda V_1 \right] \left( \frac{p}{p_0} \right)^{\frac{\kappa - 1}{\kappa}}, \quad \dots \quad (71)$$

that is, a very complicated form. If we determine from this  $dV_y$  we finally get the work of compression

$$L = \int p dV_y,$$

and, if we integrate between the corresponding limits, there finally follows

$$L = \frac{(\lambda V_1 + V_2) p_0}{\kappa - 1} \left[ \left( \frac{p}{p_0} \right)^{\frac{\kappa - 1}{\kappa}} - 1 \right] + \frac{\kappa - 1}{2\kappa - 1} \lambda V_1 p_0 \left[ \left( \frac{p}{p_0} \right)^{\frac{2\kappa - 1}{\kappa}} - 1 \right]. \quad (72)$$

For the case that the quantity of air existing in space  $B$  is forced completely into the space  $A$  we should have  $V_y = 0$ ; equation (71) then gives the pressure  $p$  at the end, by

$$\frac{p}{p_0} = \frac{\lambda V_1 + V_2}{\lambda V_1},$$

and then the foregoing equations will also permit the determination of the corresponding values of  $T_y$ ,  $L$ , and  $Q_x$ .

**Problem 3.** In the foregoing investigations it was at one time assumed that only the transfer-piston moves, and at another time that only the power-piston moves.

It is now assumed that both pistons are in motion, which leads us back to the general case represented by Fig. 30, p. 205, but for the purpose of the following investigations it seems profitable to bring the equations there given into other forms. Using Fig. 30 as a basis and the given notation, we find from equation (42), when we designate the initial pressure in both spaces by  $p_0$ , the initial temperatures by  $T_1$  and  $T_2$ , and the initial volumes of the two spaces by  $V_1$  and  $V_2$ , for the computation of the pressure  $p$ , the formula

$$\frac{p}{p_0} = \left( \frac{V_1 T_2 + V_2 T_1}{V_x T_y + V_y T_x} \right) \frac{T_x T_y}{T_1 T_2}, \quad . \quad . \quad . \quad . \quad . \quad (73)$$

and the external work  $L$  can be found by integration of the equation

$$dL = p d(V_x + V_y). \quad . \quad . \quad . \quad . \quad . \quad (74)$$

Now if  $A$  is the discharging space and  $B$  the receiving space, the heat  $Q_x$  can be found from equations (47) and (38) to be

$$dQ_x = \frac{\kappa}{\kappa - 1} A V_x p \left[ \frac{dT_x}{T_x} - \frac{\kappa - 1}{\kappa} \frac{dp}{p} \right], \quad . \quad . \quad . \quad . \quad (75)$$

and from equation (48) and equation (39), after suitable reduction, we get

$$dQ_y = \frac{\kappa}{\kappa - 1} \frac{A V_y p}{T_y} \left[ \frac{T_x dT_y}{T_y} - \left( \frac{\kappa T_x - T_y}{\kappa} \right) \frac{dp}{p} + (T_y - T_x) \frac{dV_y}{V_y} \right]. \quad (76)$$

These formulas assume that  $A$  is a discharging space, which is the case when

$$d \left( \frac{V_y}{V_x} \frac{T_x}{T_y} \right) > 0, \quad . \quad . \quad . \quad . \quad . \quad (77)$$

as was proved on p. 204.

If the inequality (77) is not fulfilled, the space  $B$  becomes the discharging space; we must then, in the two preceding formulas, everywhere interchange subscript  $x$  with subscript  $y$ .

Let us now discuss as a special case that one in which the temperature is constant in the two spaces, in which therefore  $T_x = T_1$  and  $T_y = T_2$ , an assumption which has several times been the basis of investigations of hot-air engines. If we again designate the constant ratio  $T_2:T_1$  by  $\lambda$ , then the foregoing equations give the following expressions:

$$\frac{p}{p_0} = \frac{\lambda V_1 + V_2}{\lambda V_x + V_y}, \quad . . . . . (73a)$$

$$dQ_x = -A V_x dp, \quad . . . . . (75a)$$

$$dQ_y = \frac{\kappa}{\kappa - 1} A V_y p \left( \frac{\lambda - \kappa}{\lambda \kappa} \frac{dp}{p} + \frac{\lambda - 1}{\lambda} \frac{dV_y}{V_y} \right), \quad . . . (76a)$$

which presupposes that  $A$  is the receiving space; hence

$$d\left(\frac{V_y}{V_x}\right) < 0. \quad . . . . . (77a)$$

*Special case a.* During the motion of the two pistons the pressure remains constant in the two spaces.

From equation (73a) and because  $p = p_0$  it follows that

$$V_y = V_2 + \lambda V_1 - \lambda V_x \quad . . . . . (78)$$

and

$$\frac{V_y}{V_x} = \frac{V_2 + \lambda V_1}{V_x} - \lambda,$$

from which

$$d\left(\frac{V_y}{V_x}\right) = - (V_2 + \lambda V_1) \frac{dV_x}{V_x^2}.$$

Therefore if  $A$  is the discharging space, according to equation (77a)  $dV_x$  must be negative, i.e., space  $V_x$  must decrease and hence, according to equation (78),  $V_y$  must increase; because  $V = V_x + V_y$  the latter equation gives also the total volume:

$$V = V_2 + \lambda V_1 - (\lambda - 1) V_x.$$

Accordingly this volume experiences a decrease (the power-piston like the transfer-piston [Fig. 30] moves from right

to left) when  $\lambda < 1$  or  $T_2 < T_1$ , i.e., when the higher temperature exists to the left of the transfer-piston, on the other hand the power-piston is moved from left to right when  $T_2 > T_1$  is assumed. The outer work is found from equation (74)

$$L = (V - V_0)p_0 = (\lambda - 1)(V_1 - V_x)p_0.$$

Finally the quantity of heat which must be imparted to the discharging space  $A$ , is, with  $dp = 0$ , found from equation (75a) to be

$$Q_x = 0,$$

and the heat for the receiving space, according to equation (76a), is

$$Q_y = \frac{\kappa(\lambda - 1)}{\lambda(\kappa - 1)} A(V_y - V_2)p_0 = \frac{\kappa(\lambda - 1)}{\kappa - 1} A(V_1 - V_x)p_0,$$

or also

$$Q_y = \frac{\kappa}{\kappa - 1} AL,$$

which equation can easily be expressed in words.

*Special case b.* The temperatures in both spaces are again constant, but both pistons move uniformly from left to right.

Let  $c_1$  be the velocity of the transfer-piston and  $c$  that of the power-piston, then if  $F$  represents the cross-section of both pistons, we have, at the time  $t$ ,

$$V_x = V_1 + Fc_1t$$

and

$$V = V_0 + Fct,$$

and accordingly, by subtraction,

$$V_y = V_2 + F(c - c_1)t.$$

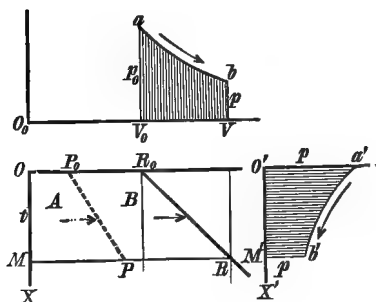


FIG. 34.

The combination of these equations furnishes

$$\frac{V_y}{V_x} = \frac{V_0 - \frac{c}{c_1} V_1}{V_x} + \frac{c - c_1}{c_1},$$

and accordingly

$$d\left(\frac{V_y}{V_x}\right) = -\left(V_0 - \frac{c}{c_1}V_1\right)\frac{dV_x}{V_x^2}.$$

Now assuming that  $A$  is the discharging space, the right member must be positive according to (77a); this requires, since  $V_x$  was assumed to increase, the fulfillment of the condition

$$\frac{c_1}{c} < \frac{V_1}{V_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (77b)$$

If we designate  $c_1 : c$  by  $m$  and eliminate the time from the three equations found for  $V_x$ ,  $V$ , and  $V_y$ , there results

$$V_x = V_1 + m(V - V_0),$$

$$V_y = V_2 + (1 - m)(V - V_0),$$

so that both magnitudes are expressed in terms of the total volume  $V$ ; the substitution in equation (73a) then gives the value of  $p$  expressed in terms of  $V$ , and consequently gives the course of the pressure curve  $ab$ , whereupon, by integration, equation (74) easily determines the external work performed.

The quantities of heat  $Q_x$  and  $Q_y$  can also be easily determined with the help of equations (75a) and (76a). There is no difficulty whatever in making the whole calculation, but we will here omit furnishing the results of the computation because very complicated expressions occur and the problem is of subordinate technical importance.

**Supplement.** The foregoing problem was principally discussed in order to indicate in conclusion how the problem is to be handled (under the like assumption that the temperature is kept constant in both spaces) when the two pistons do not move uniformly, i.e., when the given piston-diagram has the character of that shown in Fig. 30, p. 205. If the two spaces  $V_x$  and  $V_y$  are given as functions of the time, so that

$$V_x = f'(t) \quad \text{and} \quad V_y = f''(t),$$

there follows

$$V = f'(t) + f''(t).$$

Eliminating the time  $t$  from these equations,  $V_x$ , and  $V_y$  as well, can be expressed by the total volume  $V$ . Substituting these quantities in equation (73a) will give the relation for the pressure curve  $ab$ , and then the heat quantities  $Q_x$  and  $Q_y$  can be computed from formulas (75a) and (76a) by integration between the corresponding limits.

The velocities  $c_1$  and  $c$  are then variable and can be expressed by

$$c_1 = \frac{dV_x}{dt} \quad \text{and} \quad c = \frac{dV}{dt},$$

and the condition that  $A$  be the discharging space requires, according to equation (77b), that during the course of the pressure curve (for which the integration of equations (75a) and (76a) is to be effected) the relation

$$\frac{c}{c_1} < \frac{V_x}{V}$$

must be satisfied; the last two equations are to be interchanged from the moment in which

$$\frac{c_1}{c} > \frac{V_x}{V}.$$

We have to do with the last indicated case in certain, constructed, air engines—a problem to which we will return.

### III. Flow and Efflux of Gases.

#### § 40. FUNDAMENTAL FORMULAS FOR THE FLOW OF A FLUID.

In discussing the general problem of Hydrodynamics difficulties are met which up to the present time could only partially be overcome. To be sure they are not removed when the laws of Thermodynamics are employed in treating the question. Nevertheless extensions result which have become important for certain technical problems belonging to this field.

Let us first assume that a fluid of the liquid or gaseous variety flows through a horizontal pipe (Fig. 35), possessing a variable cross-section, and flows without any action on the part of external forces; let us here assume a permanent or normal condition, and consequently that in a unit of time the same weight  $G$  flows through every cross-section. Let us assume a further limitation, namely, that through every element of the forward cross-section  $F$  the liquid flows with the same velocity  $w$  and that the direction of the velocities in all

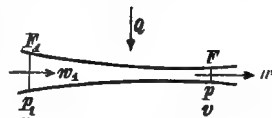


FIG. 35.

points of the cross-section are parallel, so that the volume of the fluid which passes the cross-section  $F$  in one second is represented by  $Fw$ ; similarly this volume is given by  $F_1w_1$  for the back section  $F_1$ . If  $v$  is the specific volume and  $p$  the pressure in the forward cross-section, and if we designate these same quantities for the cross-section  $F_1$  by  $v_1$  and  $p_1$ , then first of all we get for the normal condition the two relations

$$Gv_1 = F_1w_1 \quad \text{and} \quad Gv = Fw. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now let us follow the unit of weight of fluid on its path from  $F_1$  to  $F$ . Disregarding the present problem at first, let us suppose the unit of weight of fluid of volume  $v$  and pressure  $p$  to be enclosed in a vessel possessing no weight, and let  $U$  be the whole amount of the



inner work; now if this vessel is supposed to progress in space in a rectilinear and uniform fashion with a velocity  $w$ , then the value  $\frac{w^2}{2g}$  will be added to the store of work; let us designate this value by  $H$ , then if

$$H = \frac{w^2}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the term  $H$  will designate that part of the total energy which corresponds to the visible progressive motion, and the whole amount of work contained in the unit of weight will therefore be  $U + H$ . Returning to the present problem, the passage from the cross-section  $F_1$  to the cross-section  $F$  involves taking up an amount of work

$$(U + H) - (U_1 + H_1),$$

where the difference  $H - H_1$  can be designated as the energy of flow. But on the way from  $F_1$  to  $F$  there will be also resistances to overcome which, in the main, consist in friction of the fluid along the walls of the vessel; let us designate by  $W$  the loss of work thus occasioned when referred to the unit of weight of the fluid, then the whole amount of work consumed on the way  $F_1F$ , which we will temporarily designate by  $L$ , is

$$L = (U + H) - (U_1 + H_1) + W, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

but still another expression can be established for this quantity of work.

During the onward motion of the fluid body  $F_1F$  the back area,  $F_1$ , travels the distance  $w_1 dt$ , and the forward area the distance  $w dt$ . Now since  $F_1 p_1$  is the pressure which the part of the fluid following cross-section  $F_1$  exerts on the fluid body  $F_1F$ , the latter will receive at this back area from the flowing fluid the work  $F_1 w_1 p_1 dt$ , and the fluid body will exert at the forward area  $F$  the work  $F w p dt$  on the fluid preceding it. From this follows that the fluid body  $F_1F$  has taken up in the time  $dt$  the work expressed by

$$F_1 w_1 p_1 dt - F w p dt = (p_1 v_1 - p v) G dt,$$

when account is taken of equation (1). But in the time  $dt$  the weight  $Gdt$  of the fluid has entered into the space  $F_1F$ , and the same weight has passed out through the area  $F$ ; as we are considering the permanent or normal condition, the whole fluid body lying between  $F_1$  and  $F$  experiences no change in its state of motion, consequently the preceding expression can be regarded as the work which the weight  $Gdt$  of the fluid has taken up during its motion from  $F_1$  to  $F$ . For the finite time  $t^1$  this quantity of work amounts to

$$(p_1v_1 - pv)Gt,$$

and if we assume a unit of weight of fluid, that is,  $Gt=1$ , then the amount of work taken up by the unit of weight is

$$(p_1v_1 - pv).$$

Let us now further assume that during the motion from  $F_1$  to  $F$  the unit of weight of fluid has imparted to it from the outside the quantity of heat  $Q$ ; but because on its way the above indicated work of resistance  $W$  is converted into heat, the result is, on the whole, as if the quantity of heat  $Q + AW$  had been supplied. This quantity of heat expressed in work (that is, divided by  $A$ ) and combined with the already calculated quantity of work now gives, for the total quantity of work  $L$  imparted to the unit of weight of fluid on the way  $F_1F$ , the expression

$$L = p_1v_1 - pv + \frac{Q}{A} + W. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equating this with expression (3) we get the first fundamental equation for the present problem in the form

$$Q = A[pv - p_1v_1 + (U + H) - (U_1 + H_1)], \quad . \quad . \quad . \quad (5)$$

---

<sup>1</sup> In the following investigations the letter  $t$  has been used to designate the time that has elapsed, as is customary, although the same letter is also used in the present work to designate the temperature according to Celsius [Fahrenheit]. But confusion is here avoided by always expressing the temperature, in the investigations of the present chapter, in absolute measure, by  $T$ .

or passing to the differential:

$$dQ = A[d(pv) + dU + dH]. \quad . \quad . \quad . \quad . \quad (5a)$$

First of all it is remarkable that the work of resistance no longer occurs in this equation, and therefore the equation is valid no matter what resistances occur between  $F_1$  and  $F$  and what the character of these resistances may be. Generally we have to do with the friction of the fluid along the walls of the vessel, but this work of resistance may also consist in the loss of work caused by the formation of eddies, such as would arise if there were sudden changes of cross-section between the areas  $F_1$  and  $F$ . Equation (5) is untouched by such assumptions, provided the condition is satisfied that in the two limiting sections  $F_1$  and  $F$  parallelism is maintained in the directions of the velocities, provided, therefore, that in the forward section  $F$  the visible eddying motion of the fluid particles, which may have arisen between  $F_1$  and  $F$ , has disappeared. We must further remark that equation (5) remains unchanged in whatever manner and according to whatever law the total quantity of heat  $Q$  is imparted or withdrawn, as the case may be, from the unit of weight of fluid on its way from  $F_1$  to  $F$ .

Only in one direction may the equation under certain circumstances experience an extension; it was derived under the hypothesis that no external forces were exerted on the elements of the fluid; but under all circumstances, at least the force of gravity will act, and therefore equation (5) is only valid for a horizontal conduit as was assumed at the very start. If this latter condition is not satisfied, then in general it is necessary to take account of the action of the force of gravity. Let us

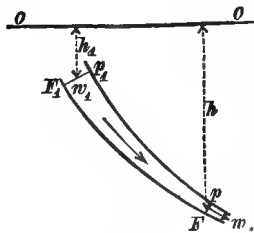


FIG. 36.

assume for this purpose that the back section  $F_1$  (Fig. 36) lies at the distance  $h_1$ , and the section  $F$  at the distance  $h$ , below the horizontal plane  $OO$ , then, in consequence of the action of the force of gravity, the unit of weight of the fluid will take up the additional work

$$h - h_1,$$

and this value should be added to the right member of equation (4); a combination with equation (3) then gives in place of equation (5) the formula

$$Q = A[pv - p_1v_1 + (U + H) - (U_1 + H_1) - (h - h_1)], \quad . \quad . \quad (I)$$

or, passing to the differential,

$$dQ = A[d(pv) + dU + dH - dh]. \quad . \quad . \quad . \quad (Ia)$$

Finally we must emphasize, and this appears from the whole presentation, that, strictly speaking, the foregoing propositions apply only to the motion of the fluid in a conduit possessing an infinitesimal cross-section variable though it be; when applying the equation obtained to the case of finite cross-sections we enter the realm of approximate computations.<sup>1</sup>

In addition to the equations already developed, among which we will always choose the differential equation (Ia) for the sake of simplifying the coming investigations, there is still another, second, relation between the introduced quantities, which is furnished by the fundamental equation (8), p. 23, of Thermodynamics; in the latter equation we must, besides the quantity of heat  $Q$  supplied from the outside, take account of the quantity of heat  $AW$  developed by the work of resistance  $W$ ; consequently

$$Q + AW = A(U - U_1) + A \int_{v_1}^v p dv, \quad . \quad . \quad . \quad (II)$$

---

<sup>1</sup> The different forms in which equation (I) occurs in the text can easily be brought into the form in which it is to be applied when any external forces act on the fluid element, provided these forces can be regarded as derived from a force function  $V$ . Let  $x$ ,  $y$ , and  $z$  be the coordinates of a fluid element referred to rectangular coordinates at the time  $t$ , and let  $X$ ,  $Y$ , and  $Z$  be the three force components acting on the unit of weight of the fluid; then, as is well known,

$$dV = Xdx + Ydy + Zdz$$

is the differential of the work of these forces. We then simply substitute  $dV$  for  $dh$  in equation (Ia), so that we get

$$dQ = A[d(pv) + dU + dH - dV],$$

or integrated,

$$Q = A[pv - p_1v_1 + U - U_1 + H - H_1 - (V - V_1)],$$

where  $V - V_1$  represents the part of the work which the unit of weight of fluid has received on the way  $F_1F$  (Fig. 36) from the external forces.

or

$$dQ + AdW = A(dU + pdv). \quad \text{. . . . . (IIa)}$$

The two equations (I) and (II) now furnish the basis for a full investigation of the flow of fluids under the prescribed limitations.<sup>1</sup>

The combination of equations (I) and (II) or (Ia) and (IIa) furthermore leads to the following expressions,<sup>2</sup> whose use, in certain cases, simplifies the calculation:

$$H - H_1 = h - h_1 - W - \int_{p_1}^p v dp, \quad \text{. . . . . (III)}$$

$$dH = dh - dW - v dp. \quad \text{. . . . . (IIIa)}$$

In practical applications it is almost exclusively a question of determining the energy of flow  $H$ , and then, by means of equation (2), the velocity  $w$  in the cross-section is found by the formula

$$w = \sqrt{2gH},$$

and the weight  $G$  of the fluid passing in one second through the cross-section is determined according to equation (1) from

$$G = \frac{Fw}{v}. \quad \text{. . . . . (IV)}$$

It is worthy of note that the integral

$$-\int_{p_1}^p v dp = p_1 v_1 - pv + \int_{v_1}^v p dv \quad \text{. . . . . (6)}$$

<sup>1</sup> I first called attention to the connection of hydrodynamic equations with those of thermodynamics in my treatise, "Das Lokomotivenblasrohr. Experimentelle und theoretische Untersuchungen über die Zugerzeugung durch Dampfstrahlen und die saugende Wirkung der Flüssigkeitsstrahlen überhaupt," Zurich, 1863. I there developed new formulas for the efflux of vapors and pointed out the connection which existed between the different formulas, which up to that time had been given for the efflux of gases. See also the author's articles "Ausfluss von Dämpfen und hocherhitzten Flüssigkeiten aus Gefässmündungen," *Civilingenieur*, Vol. 10, 1864, p. 87, and "Neue Darstellung der Vorgänge beim Ausströmen der Gase und Dämpfe aus Gefässmündungen," *Civilingenieur*, Vol. 17, 1871, p. 1.

<sup>2</sup> If any external forces act on the fluid element (provided of course they are derived from the force function), we must insert in equations (III) and (IIIa) in place of  $h$  and  $h_1$  the force function  $V$  and  $V_1$ , respectively, as was already emphasized in the remark on the preceding page.

occurring in equation (III) can easily be represented graphically. If we lay off, as rectangular coordinates (Fig. 37), the pressure  $p_1$  and the specific volume  $v_1$  of the fluid in the back section  $F_1$ , and likewise the corresponding values  $p$  and  $v$  belonging to the forward section  $F$ , and if we assume that the law is known according to which the pressure  $p$  varies with the volume while on the way  $F_1F$  (Fig. 36), that is, assume the course of the curve  $ab$  as known, then the hatched area in Fig. 37 represents the value of the preceding integral and consequently determines the value

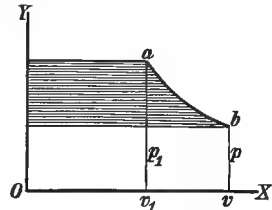


FIG. 37.

$$-\int_{v_1}^v v dp = H - H_1 - (h - h_1) + W, \quad . \quad . \quad . \quad (6a)$$

in accordance with equation (III).

The formulas developed still hold for other kinds of fluid; with liquid fluids in which, for widely separated pressure limits, the specific volume can be regarded as constant, so that we may write  $v = v_1$  and  $dv = 0$ , equation (III) gives with the help of equation (2) the formula

$$\frac{w^2 - w_1^2}{2g} = h - h_1 - W + v_1(p_1 - p),$$

one long known in Hydraulics; but hitherto equation (I) or (II) has not been considered in such investigations.

## § 41. THE FLOW OF GASES.

In applying the foregoing fundamental equations to the motion of gases, equation (III) remains unchanged in form. On the other hand the two equations (I) and (II) from which equation (III) was derived experience remarkable simplification. The change  $dU$  of energy is given, for gases, by the relation (51), p. 132,

$$dU = \frac{d(pv)}{\kappa - 1},$$

substitution in equation (Ia) therefore gives

$$AdH = dQ - \frac{A\kappa}{\kappa - 1}d(pv) + Adh, \quad . \quad . \quad . \quad . \quad . \quad (Ib)$$

and from equation (IIa) follows

$$dQ + AdW = \frac{A}{\kappa - 1}(vdp + \kappa pdv). \quad . \quad . \quad . \quad . \quad (IIb)$$

If we introduce the temperature  $T$  into equation (Ib) by utilizing the equation of condition  $pv = BT$ , and also the relation

$$c_p \frac{\kappa - 1}{\kappa} = AB,$$

which was found upon p. 134, there will follow

$$AdH = dQ + AdH - c_p dT, \quad . \quad . \quad . \quad . \quad . \quad (Ic)$$

and similarly equation (IIb) can be brought into other forms if we consider the different equations (53), pp. 133 and 134.

It is noticeable that the introduction of temperature  $T$  gives a very simple form of equation (Ic), but it deserves to be emphasized that an experimental determination of the temperature of flowing gases, of flowing fluids generally, is not possible, at least with the help of thermometers, because friction and the impact of the fluid against the bulb influences the reading of the thermometer.

We should note that in most writings on Physics and Mechanics, until very recently, equation (IIIa) given above has been exclusively employed in the solution of hydrodynamic problems, and, when integrating the last term  $vdp$  of the right member of the equation, different hypotheses were assumed with regard to the relation between the quantities  $p$  and  $v$ ; but as the equation may be regarded as derived from equations (I) and (II), each of these hypotheses can always be regarded as a particularly definite assumption with respect to the quantity of heat  $dQ$  to be imparted to the fluid, and with respect to the law to which the resistances are subjected; not until there is a simultaneous consideration of

these circumstances does one gain complete insight into the occurrences. It is judicious, when investigating certain cases, to choose as a starting-point the two fundamental formulas (Ia) and (IIa), and in gases to use the corresponding equations (Ib) and (IIb).

## § 42. EFFLUX OF GASES UNDER CONSTANT PRESSURE THROUGH SIMPLE ORIFICES.

Let us suppose a very large vessel filled with atmospheric air of pressure  $p_1$ , temperature  $T_1$ , and specific volume  $v_1$ , but provided with an orifice of efflux through which the air streams into a second space in which prevails the pressure  $p_2$ , which is likewise kept at a constant height; the condition that the pressure  $p_1$  in the discharging vessel is kept constant is satisfied if we suppose that simultaneously vessel and receiver are of great capacity, and that the orifice of efflux has a very small cross-section and that relatively the period of efflux is a small one. The ordinary case, which will at first be assumed in what follows, is the flow of air into the free atmosphere; in the plane of the orifice (Fig. 38) whose cross-section amounts to  $F$  square meters [square feet] the pressure  $p$  prevails, and at first we will assume that it is different from the external pressure  $p_2$ ; let the temperature and specific volume in the plane of the orifice be  $T$  and  $v$  and outside of it be  $T_1$  and  $v_2$ , then the temperature in this orifice will be identical with that in the discharging vessel.

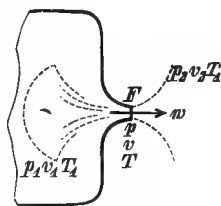


FIG. 38.

Finally, in order to ignore for the present the influence of the contraction of the air-jet, suppose the orifice to be rounded on the inside. The problem which is now before us consists in determining the energy of flow  $H$  in the plane of the orifice and in determining the velocity of the efflux  $w$  and the discharge  $G$  per second measured in kilograms [pounds], for which latter purposes equations (2) and (IV) are to be employed.

In the large discharging vessel the air is assumed to be in a state of rest, and therefore  $H_1 = 0$ , because  $w_1 = 0$ ; if the jet flows





pressure of the air varies with the volume while the air in the discharging vessel flows from a state of rest towards the orifice, a motion which doubtless, as indicated in Fig. 38, occurs in a funnel-shaped space; similarly the air outside of the orifice spreads itself, passing from the velocity  $w$  to a state of rest.

In the latter case, after the spreading, we have in the receiving vessel  $H=0$ , and because, in the discharging vessel itself,  $H_1=0$  we have generally, from equation (I),

$$Q=A[p_2v_2-p_1v_1+U_2-U_1-(h_2-h_1)], \quad . \quad . \quad . \quad (10)$$

where the values possessing the subscript 2 relate to the state of the air after spreading, i.e., to the final condition of rest.

If, as is assumed, heat supply from without does not occur, so that  $Q=0$ , and if the jet of air flows out vertically upwards, then  $h_2-h_1$  represents the rise.

For horizontal efflux there follows from the preceding formula

$$0=p_2v_2-p_1v_1+U_2-U_1, \quad . \quad . \quad . \quad . \quad (11)$$

or

$$d(pv)+dU=0. \quad . \quad . \quad . \quad . \quad . \quad (11a)$$

If, as is the case throughout this work, we consider air as a perfect gas, then for  $U$  we must employ equation (52), p. 132, and therefore follows

$$p_2v_2=p_1v_1,$$

or, with the help of the equation of condition,

$$T_2=T_1,$$

i.e., the quantity of discharged air, after spreading outside, again possesses the same temperature as in the discharging vessel, whatever resistances may have obtained during the efflux and whatever pressure  $p$  may prevail in the plane of the orifice,—so long as the condition is fulfilled that the air (during horizontal efflux) neither receives nor rejects heat during its flow toward the orifice. As the air, in accordance with our

assumption, already possesses the temperature  $T_1$  on the outside, the air thus added does not change this temperature.

Now to be sure this proposition is only approximately true, as W. Thomson and Joule have already shown by experiment (in 1862).<sup>1</sup> In reality  $T_2 < T_1$ , but the fall of temperature is so slight that it can be disregarded, particularly in the investigations on the efflux of gases. The deviations are due to the fact that with real gases equation (52), p. 132, for the inner work or energy  $U$ , is only an approximation. The experiments adduced have not been disregarded in works on Physics and in articles on Thermodynamics, but it was reserved for Linde, starting from these results, to practically, in a clever fashion, realize his procedure for the liquefaction of air. Later on, when investigating the behavior of air as vapor, we will discuss this question more fully.

After this preliminary we will now return to the efflux problem.

To decide the question how the pressure  $p_1$  in the discharging vessel changes with the pressure  $p$  in the plane of the orifice, we must use equation (IIc), which serves for the calculation of the work of resistance  $W$ . If we first assume that the resistances to be overcome by the flowing air in the orifice can be neglected as infinitesimal, then  $dW = 0$ ; we therefore get from equation (IIc)

$$vdp + \kappa p dv = 0,$$

and from this by integration

$$pv^\kappa = p_1 v_1^\kappa; \quad . . . . . (12)$$

consequently the expansion curve is the adiabatic line. If we determine from this relation the quantity  $v$ , and substitute it in equations (8) and (9), we get for the present case

$$v = \sqrt{\frac{2g\kappa}{\kappa-1}} p_1 v_1 \left[ 1 - \left( \frac{p}{p_1} \right)^{\frac{\kappa-1}{\kappa}} \right] \quad . . . . . (13)$$

and

$$G = F \sqrt{\frac{2g\kappa}{\kappa-1}} \frac{p_1}{v_1} \left[ \left( \frac{p}{p_1} \right)^{\frac{2}{\kappa}} - \left( \frac{p}{p_1} \right)^{\frac{\kappa+1}{\kappa}} \right] \quad . . . (14)$$

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<sup>1</sup> W. Thomson and Joule, Philos. Transactions of the Royal Society of London, 1862.

These two formulas were first given by de Saint Venant and Wantzel<sup>1</sup> (1839) and then, later, were also derived by Weisbach,<sup>2</sup> who doubtless did not know about the older experiments. De Saint-Venant and Wantzel, as well as Weisbach, sought to test the equations by experiments on the efflux of air and tried to determine the corrections which must be applied to the formulas in order to effect an agreement of the experiments with the calculations. But the experimental results of de Saint-Venant and Wantzel are exceedingly unreliable, for reasons already discussed in § 36, p. 186, and, in part, mentioned by Poncelet. Moreover the said investigators finally forsook the formulas and gave, in their place, approximate expressions which reproduced the results of their experiments, and thereafter the formulas received no further consideration from others.

The two French engineers deserve the credit of subjecting to a closer examination the two equations (13) and (14), and of first discussing the question whether, and under what conditions, the pressure  $p$  in the orifice could be taken as identical with the external pressure  $p_2$ , a question which for a long time received no attention, like the whole article of de Saint Venant and Wantzel; not until 1860 did Max Herrmann<sup>3</sup> treat the question in the same way as the French writers, doubtless without knowing about their work; whereupon Kolster<sup>4</sup> (1867) went into the subject more thoroughly, referring, in so doing, to the French writers. The first and complete experiments on efflux of air we owe to Weisbach; he<sup>5</sup> designated the velocity  $w$  and the discharge  $G$  as "theoretical values," because

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<sup>1</sup> See reference on p. 186.

<sup>2</sup> Weisbach, "Lehrbuch der Ingenieur- und Maschinenmechanik." 3d, edition, 1855, Vol. 1, p. 820.

<sup>3</sup> Zeitschrift des österreichischen Ingenieurvereins, 1860, Jan. 12, p. 34.

<sup>4</sup> Kolster, "Über das Ausströmen von Dampf und Luft." Zeitschrift des Vereins deutscher Ingenieure, Vol. XI, 1867, p. 435.

<sup>5</sup> Weisbach, "Vorläufige Mittheilungen über die Ergebnisse vergleichender Versuche über den Ausfluss der Luft und des Wassers unter hohem Druck," Civilingenieur, Vol. 5, 1859, p. 1; also "Versuche über Ausströmung der Luft unter hohem Druck durch Mundstücke und Röhren," Civilingenieur, Vol. 12, 1866, pp. 1 and 77.

the two formulas (13) and (14) were developed by neglecting the resistances, and he determined the real or effective velocity of efflux, which we designate by  $w_e$  and which is smaller than  $w$ , by the relation

$$w_e = \phi w,$$

where  $\phi$  was introduced as the velocity coefficient, as is customary in practical hydraulics.

The effective energy of flow  $H_e$  in the plane of the orifice would consequently be

$$H_e = \phi^2 H,$$

and the work of resistance  $W$ ,

$$W = H - H_e = (1 - \phi^2)H = \left(\frac{1}{\phi^2} - 1\right)H_e = \zeta H_e, \quad . \quad . \quad (15)$$

provided we introduce the notation

$$\zeta = \frac{1}{\phi^2} - 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The value  $\zeta$  is designated as "the coefficient of resistance," according to Weisbach, to whom we owe the introduction of this factor into the formulas of practical hydraulics and at the same time its experimental determination for different kinds of resistances. Working backward from equation (16) we get the velocity coefficient

$$\phi = \sqrt{\frac{1}{1 + \zeta}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and, as soon as it is known, equation (13) gives the effective efflux velocity  $w_e$  if one multiplies the radical on the right side by  $\phi$ .

With orifices well rounded on the inside, and with short, cylindrical adjutages, in each of which the jet leaves the orifice with its full cross-section, we get the true discharge  $G_e$  from

$$G_e = \phi G,$$

where  $G$  is determined from equation (14); on the other hand, if there are contractions, as with orifices in a thin wall, we must

substitute for the cross-section  $F$  of the orifice, the cross-section  $\alpha F$  at the place of greatest contraction, in which case the factor  $\alpha$ , the "coefficient of contraction," must be determined by experiment. In this case we should have

$$G_e = \mu G,$$

where  $\mu$  represents the "coefficient of efflux," which equals the product  $\alpha\phi$ .

The beautiful experiments of Weisbach were carried out on a large scale and were in part re-calculated by Grashof<sup>1</sup>; they were only intended to determine the coefficients  $\phi$  and  $\mu$  for a series of different forms of orifices. In general it turned out that these coefficients (at least within the limits employed by Weisbach) deviated but little from those observed during the efflux of water, likewise mostly found by Weisbach; moreover for one and the same orifice the velocity coefficient  $\phi$  and the coefficient of resistance  $\zeta$  proved to be nearly invariable for various differences of pressure; these results had, indeed, already been accepted, on the basis of older experiments conducted by Schmidt (1820), Lagerhjelm (1822), Koch (1824), and d'Aubuisson (1826); the latter experiments, to be sure, were carried on throughout with very slight excess of pressure (fraction of one meter of water column); it was Weisbach who first went up to one atmosphere excess of pressure. Later on there will be an opportunity of coming back to Weisbach's experimental results (this experimental method has already been discussed on p. 191); here we need only remark that Weisbach omitted such a discussion of equations (13) and (14) as was undertaken by de Saint Venant and Wanzel, and assumed from the start that in his experiments the pressure  $p$  in the plane of the orifice was identical with the pressure  $p_2$  of the external atmosphere. The assumption is correct for the pressures used by Weisbach; it will be shown that the assumption would not have been permissible in calculating the experiments if the pressure in the discharging vessel had been a little larger than it really was.

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<sup>1</sup> Grashof, "Theoretische Maschinenlehre," Vol. 1, Leipsic, 1875.

### § 43. DISCUSSION OF THE EFFLUX FORMULAS.

In the two equations (13) and (14) the state of the air ( $p_1$  and  $v_1$ ) in the discharging vessel is regarded as known; likewise the cross-section  $F$  of the orifice measured in square meters [square feet]. Then the efflux of velocity  $w$ , and the air weight  $G$  in kilograms [pounds] per second, can be computed, provided the pressure  $p$ , in the plane of the orifice, is given. Now it seems natural to assume that the pressure  $p_2$  (outside the discharging vessel) extends up to the plane of the orifice, and that therefore  $p = p_2$  may be written.

In this case equation (14) gives the quantity discharged as  $G=0$ , as must be the case provided also the pressure in the discharging vessel and in the receiving vessel is equal, that is,  $p_2 = p_1$ .

On the other hand if we suppose the flow to take place into a vacuum, and if here also the pressure  $p_2=0$  extends up to the plane of the orifice, then equation (14) would again give  $G=0$  for  $p=0$ , from which follows the absurd result that no flow takes place toward a vacuum.

One must therefore draw the conclusion that the external pressure  $p_2$  will in general not be identical with the pressure  $p$  of the orifice, or only under certain circumstances.

A closer examination of equation (14) shows that a certain value of  $p$  exists for which the discharge  $G$  is a maximum.

The differentiation of the bracketed quantity under the radical gives, as is easy to see, a maximum for

$$\frac{p}{p_1} = \left( \frac{2}{\kappa + 1} \right)^{\frac{\kappa}{\kappa - 1}}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If  $p_1$  is given, we can compute, by this formula, the corresponding pressure  $p$  in the plane of the orifice and then, with the help of equation (12), find the corresponding specific volume  $v$  there, from

$$\frac{v}{v_1} = \left( \frac{\kappa + 1}{2} \right)^{\frac{1}{\kappa - 1}}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and then also

$$\frac{pv}{p_1 v_1} = \frac{2}{\kappa + 1}. \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (20)$$

At the same time the last formula, after substitution of the absolute temperatures  $T$  and  $T_1$ , gives

$$\frac{T}{T_1} = \frac{2}{\kappa + 1}, \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (21)$$

from which the temperature  $T$  in the plane of the orifice can be computed, when that of  $T_1$  in the discharging vessel is known.

As  $\kappa = 1.410$  for atmospheric air, there follows from the preceding formulas

$$\frac{p}{p_1} = 0.5266, \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (18a)$$

$$\frac{v}{v_1} = 1.5759, \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (19a)$$

and

$$\frac{T}{T_1} = \frac{pv}{p_1 v_1} = 0.8299. \quad \cdot \cdot \cdot \cdot \cdot \quad (20a)$$

If we use relation (18) in equation (14), the maximum of discharge, which is designated by  $G_m$ , can be calculated:

$$G_m = F \left( \frac{2}{\kappa + 1} \right)^{\frac{1}{\kappa - 1}} \sqrt{\frac{2g\kappa}{\kappa + 1} \frac{p_1}{v_1}}, \quad \cdot \cdot \cdot \cdot \quad (21)$$

or with  $\kappa = 1.410$ ,

$$G_m = 2.1499 F \sqrt{\frac{p_1}{v_1}}, \quad \cdot \cdot \cdot \cdot \cdot \quad (21a)$$

$$\left[ G_m = 3.8942 F \sqrt{\frac{p_1}{v_1}} \right].$$

If we multiply both sides of this equation by  $v_1$ , then  $Gv_1$  gives the maximum of air in cubic meters [cubic feet], measured under the internal pressure, and because  $p_1 v_1 = BT$  there follows

$$G_m v_1 = 11.631 F \sqrt{T_1},$$

$$[G_m v_1 = 15.703 F \sqrt{T_1}].$$



Now if we assume the temperature of the air in the discharging vessel to be  $0^{\circ}\text{C}$ . [ $32^{\circ}\text{F}$ .], there will follow from this formula

$$\frac{G_m v_1}{F} = 192.18 [348.905].$$

Consequently when referred to a square meter [square foot] of orifice area, the maximum discharge per second, measured at the inner pressure, must be taken at 192.18 cbm. [348.905 cu. ft.], all this under the assumption which is here maintained throughout, that the air-jet leaves the orifice with full cross-section, and that therefore no contraction of the jet exists.

In order to give a general view of the variation of the discharge  $G$  with the orifice pressure  $p$ , let us lay off in Fig. 39*a* the value  $x = \frac{p}{p_1}$  as abscissa, and as ordinate the discharge  $G$  calculated from equation (14), p. 236, and thus get the curve  $oab$ ; now if the orifice pressure  $p$  were really identical with the external pressure  $p_2$ , then for the diminution of the pressure ratio  $p_2:p_1$  from the

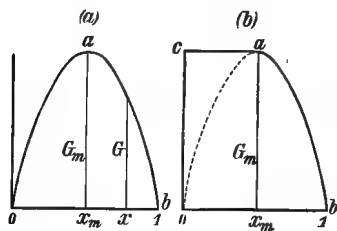


FIG. 39.

value 1 to  $x_m$  there would result, in accordance with equation (18), an increase of the discharge according to the portion of the curve  $ba$  and in entire accordance with expectation; the diminution of  $G$  would occur like that represented by the branch of the curve  $ao$ . Now because such a diminution cannot really exist de Saint Venant and Wantzel first (ibid.) set up the hypothesis that for the interval in question the curve branch  $ao$  should be replaced by a horizontal line ( $ac$ ) (Fig. 39*b*); so long, therefore, as the pressure ratio  $p_2:p_1$  lies between 0 and the value  $x_m$  given by equation (18), so long the same quantity of air will flow out, namely, that given by equation (21) or (21*a*); in this case the orifice pressure  $p$  would be different from the external pressure  $p_2$ , and indeed it would be greater and be determined by equation (18); the discharged air seems then to be independent of the external pressure within the limits indicated.

The rule for computing should therefore be as follows: There is given the internal pressure  $p_1$ , the external pressure  $p_2$ , and the efflux cross-section  $F$ , and also the temperature  $T_1$  in the discharging vessel. First compute the orifice pressure  $p$  for the maximum discharge according to equation (18), namely,

$$p = p_1 \left( \frac{2}{\kappa + 1} \right)^{\frac{\kappa}{\kappa - 1}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now if  $p_2 > p$ , we get, from equation (14), for the discharge

$$\frac{G}{F} = \sqrt{\frac{2g\kappa}{\kappa - 1} \frac{p_1}{v_1} \left[ \left( \frac{p_2}{p_1} \right)^{\frac{2}{\kappa}} - \left( \frac{p_2}{p_1} \right)^{\frac{\kappa + 1}{\kappa}} \right]}, \quad . \quad . \quad . \quad . \quad (23)$$

where  $v_1$  is to be computed from the relation  $p_1 v_1 = BT_1$ .

On the other hand, for  $p_2 < p$ , the discharge results from equation (21), namely,

$$\frac{G}{F} = \left( \frac{2}{\kappa + 1} \right)^{\frac{1}{\kappa - 1}} \sqrt{\frac{2g\kappa}{\kappa + 1} \frac{p_1}{v_1}}, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and therefore appears independent of the external pressure  $p_2$  and is valid even for efflux into a vacuum. The orifice pressure  $p$  is then determined from equation (22), whatever external pressure  $p_2$  may exist.

We reach very remarkable results if we also determine the magnitudes of the corresponding efflux velocity  $w$ . If  $p_2 > p$ , then according to equation (13) the efflux velocity is

$$w = \sqrt{\frac{2g\kappa}{\kappa - 1} p_1 v_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{\kappa - 1}{\kappa}} \right]}. \quad . \quad . \quad . \quad . \quad (25)$$

On the other hand if  $p_2 < p$ , equation (22) must be used in equation (13) and we get

$$w = \sqrt{\frac{2g\kappa}{\kappa + 1} p_1 v_1}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and is therefore also independent of the external pressure  $p_2$  and valid down to  $p_2 = 0$ .

Now if we utilize formula (20) in the last equation there also follows

$$w = \sqrt{g\kappa \cdot p v}, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where the quantities  $p$  and  $v$  refer to the cross-section of the orifice.

This equation gives nothing else than the acoustic velocity corresponding to the state of the air in the orifice. We can therefore enunciate the proposition that the efflux velocity can never be greater, even for flow into a vacuum, than the acoustic velocity belonging to the state of the air in the orifice.

The proposition is not found with de Saint Venant and Wantzel, but first with Holtzmann (1861),<sup>1</sup> who reaches the same conclusion, though in another way. With respect to the efflux of air into a vacuum, he says (ibid., p. 376):

"If the velocity of the leaving air is greater than that of the air which is flowing away in front of the efflux orifice, then an increase of density must occur in front of the efflux orifice. We know that this density is propagated with the velocity of sound. The condensation will therefore increase immediately in front of the efflux orifice so long as the velocity of efflux is greater than the velocity of sound and so long as no normal (permanent) condition occurs. This normal state will first exist when the density at the efflux orifice has become so large that the velocity of efflux is equal to the velocity of sound."

The efflux velocity of air is to be sure judged by Holtzmann on the basis of the old Navier formula, but this has no influence on his conclusions. The air-jet shows phenomena designated by E. Mach<sup>2</sup> as "stationary acoustic waves," when  $p_2 < p$ , that is, when air streams toward a vacuum or when air under a high pressure flows toward a space in which the pressure is essentially smaller (smaller than half that in the discharging vessel); this has been confirmed by photographs of the air-jet.

Recently the question has been more fully treated experimentally and analytically by Emden.<sup>3</sup>

<sup>1</sup> Dr. Carl Holtzmann, "Lehrbuch der theoretischen Mechanik," Stuttgart, 1861.

<sup>2</sup> E. Mach and E. Salcher, "Optische Untersuchung der Luftstrahlen," Wiedemann's Annalen, new series, Vol. 41, 1890, p. 144.

<sup>3</sup> Dr. Rob. Emden, "Über die Ausströmungserscheinungen permanenter Gase," Leipzig, 1899.

#### § 44. INTRODUCTION OF THE RESISTANCES INTO THE EFFLUX FORMULAS FOR SIMPLE ORIFICES. THE EFFLUX EXPONENT.

The formulas given in the foregoing determine the efflux velocity and the discharge, under the assumption that there are no resistances whatever; but in reality losses of energy do occur, even with the simplest forms of orifices, thus causing the aforesaid values, and particularly the discharge, to turn out smaller. The corresponding corrections necessary for the formulas, in order to make them agree with reality, can only be determined by special experiments; we can then proceed by the methods of Hydraulics, also employed by Weisbach for the efflux of air; in thus determining the coefficient of velocity, coefficient of resistance, and coefficient of efflux, we secure the necessary basis, in accordance with the remarks made on p. 238. There is no objection in itself to this method of calculation, but it is attended with the evil that it does not permit more exact data concerning the state of the air in the plane of the orifice, i.e., does not permit the determination of the pressure, volume, and temperature there.

The work of resistance  $W$ , calculated by equation (15) for the unit of weight, gives no clue as to the law according to which the air expands while streaming toward the orifice.

But now, in the closer investigation of this problem, we will first expressly assume that we are dealing with efflux through simple orifices and consequently, in accordance with technical Hydraulics, dealing with an orifice which is well rounded on the inside or is provided with a short, cylindrical pipe (adjutage) that has sharp edges on the inside, or, finally, dealing with an orifice in a thin wall,—always under the assumption that the orifice in question exists right in the wall of a large discharging vessel. The following propositions are no longer valid when the air flows out overcoming great resistances, for example, attains efflux through a long pipe; the latter case will be subjected to a closer examination below.

For simple orifices I proceed from the assumption that the

coefficient of resistance  $\zeta$ , introduced into equations (15) and (16), may be regarded as constant for a particular form of orifice, just as was proved by Weisbach to be true for the efflux of water.

From equation (15) then follows, if we designate the effective energy of flow by  $H$  instead of  $H_e$ :

$$W = \zeta H,$$

or if we differentiate and use equation (Ic), p. 234,

$$dW = -\frac{\kappa\zeta}{\kappa-1}d(pv). \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

On the other hand equation (IIc), p. 234, gives  $dW$  directly:

$$dW = \frac{1}{\kappa-1}(vd p + \kappa p dv).$$

Equating both expressions we therefore get the differential equation of the curve of expansion:

$$(1 + \kappa\zeta)vd p + \kappa(1 + \zeta)p dv = 0.$$

If for the sake of simplicity we substitute

$$n = \frac{\kappa(1 + \zeta)}{1 + \kappa\zeta}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

integration will give

$$pv^n = p_1 v_1^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and utilizing the equation of condition for gases there also follows

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{n-1} = \left(\frac{p}{p_1}\right)^{\frac{n-1}{n}} = \frac{pv}{p_1 v_1}, \quad . \quad . \quad . \quad . \quad (31)$$

according to which the real value of the volume  $v$  and the temperature  $T$  can be calculated from the pressure  $p$  in the orifice. As the assumption of a constant value for  $\zeta$  also makes  $n$  constant, it follows from equation (30) that the curve of expansion is the polytropic curve; for  $\zeta=0$ , i.e., neglecting the resistances, we have  $n=\kappa$ , i.e., the curve passes, as already found, into the adiabatic line. I have called the magnitude  $n$  the "efflux

exponent''<sup>1</sup>; it can easily be determined from equation (29) when  $\zeta$  is known from experiment; conversely if  $n$  is given, we get

$$\zeta = \frac{\kappa - n}{\kappa(n-1)}, \quad \dots \quad (32)$$

according to which  $n$  is always smaller than  $\kappa$ .

For the efflux of water, according to Weisbach, the coefficient of resistance  $\zeta$  for a well-rounded orifice, and also for an orifice in a thin wall, is  $\zeta=0.063$ , and for the cylindrical adjutage  $\zeta=0.505$ . If we suppose these values to be also valid for the efflux of air, we shall get respectively  $n=1.376$  and  $n=1.239$ . Now if we determine  $v$  from equation (30) and substitute it in equations (8) and (9), p. 234, there follows

$$w = \sqrt{\frac{2g\kappa}{\kappa-1}} p_1 v_1 \left[ 1 - \left( \frac{p}{p_1} \right)^{\frac{n-1}{n}} \right], \quad \dots \quad (33)$$

$$G = F \sqrt{\frac{2g\kappa}{\kappa-1}} \frac{p_1}{v_1} \left[ \left( \frac{p}{p_1} \right)^{\frac{2}{n}} - \left( \frac{p}{p_1} \right)^{\frac{n+1}{n}} \right], \quad \dots \quad (34)$$

according to which  $w$  and  $G$  can be calculated, when the pressure  $p$  in the orifice is known; moreover, for this case the temperature  $T$  in the orifice can be found from equation (31), and if we employ the equation of condition, in the sometimes used form

$$Ap_1 v_1 = c_p \frac{\kappa-1}{\kappa} T_1,$$

we get from equation (33) the energy of flow  $H$  in the orifice (measured in units of heat)

$$AH = A \frac{w^2}{2g} = c_p (T_1 - T), \quad \dots \quad (33a)$$

and the resistance, measured in like manner,

$$AW = \zeta \cdot c_p (T_1 - T).$$

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<sup>1</sup> "Neue Darstellung der Vorgänge beim Ausströmen der Gase und Dämpfe aus Gefässmündungen," Civilingenieur, Vol. 17, 1871, p. 71.

We must now decide the question as to what pressure  $p$  prevails in the plane of the orifice, when the pressure  $p_2$  is given in the receiving vessel. Here also it is shown by equation (34) that a certain value of  $p:p_1$  exists for which the discharge  $G$  is a maximum, and indeed we get, from equation (34), by differentiation of the bracket under the radical, the corresponding ratio  $x_m$  and find it equal to

$$x_m = \frac{p}{p_1} = \left( \frac{2}{n+1} \right)^{\frac{n}{n-1}}. \quad . \quad . \quad . \quad . \quad . \quad (35)$$

From the equation of the polytropic curve  $pv^n = p_1v_1^n$  we also find

$$\frac{v}{v_1} = \left( \frac{n+1}{2} \right)^{\frac{1}{n-1}}. \quad . \quad . \quad . \quad . \quad . \quad (36)$$

If we substitute the value of  $x_m$  from equation (35) in equation (33), we get, when there is a maximum discharge, for the velocity of efflux,

$$w = \sqrt{\frac{2g\kappa}{\kappa-1} \left( \frac{n-1}{n+1} \right) p_1 v_1}, \quad . \quad . \quad . \quad . \quad . \quad (37)$$

and then, with the help of the relation  $G_mv = Fw$  and equation (36),

$$G_m = \left( \frac{2}{n+1} \right)^{\frac{1}{n-1}} \cdot \sqrt{\frac{2g\kappa}{\kappa-1} \left( \frac{n-1}{n+1} \right) \frac{p_1}{v_1}}, \quad . \quad . \quad . \quad . \quad (38)$$

which two equations, when  $n = \kappa$ , i.e., when resistances are neglected, pass over into equations (26) and (24), p. 243.

If we should here also use the rule of de Saint Venant and Wanzel, as I did in earlier articles and former editions of this book, then the foregoing formulas would also be valid for efflux into a vacuum.

Therefore if  $p_1$ ,  $v_1$ ,  $n$ , and the pressure  $p_2$  in the receiving vessel are given, we must carefully observe whether the ratio  $p_2:p_1$  is greater or smaller than the value of  $x_m$  given by equation (35); if it is greater,  $w$  and  $G$  must be calculated from equations (33) and (34); if it is smaller, equations (37) and (38) are to be employed.

But with simple orifices, for which the efflux exponent  $n$  is always just a little smaller than  $\kappa$ , equation (37) gives values for the efflux velocity in the orifice, so that it seems natural to assume that the two values are here also identical.

New experiments, with great resistances in long pipes, which will be discussed below, confirm this assumption, therefore in subsequent investigations I proceed from the new hypothesis:

“that the air flows into the vacuum with the acoustic velocity

$$w = \sqrt{g\kappa pv}, \quad . . . . . (39)$$

corresponding to the state of the air in the orifice, no matter what resistances exist during the flow toward the orifice,”

a proposition which may have a great range for certain technical investigations.

If we return to the fundamental equation (8), p. 234, we get, with the help of equation (39),

$$pv = \frac{2}{\kappa + 1} p_1 v_1. \quad . . . . . (40)$$

Equation (39) gives no clue concerning the values  $p$  and  $v$  in the orifice; but if, for such simple orifices as those above, we proceed on the assumption that the expansion of the air takes place polytropically, we get, from the relation  $pv^n = p_1 v_1^n$ ,

$$\frac{pv}{p_1 v_1} = \left( \frac{p}{p_1} \right)^{\frac{n-1}{n}},$$

and therefore, by combining with equation (40),

$$x_m = \frac{p}{p_1} = \left( \frac{2}{\kappa + 1} \right)^{\frac{n}{n-1}}, \quad . . . . . (41)$$

also

$$\frac{v}{v_1} = \left( \frac{\kappa + 1}{2} \right)^{\frac{1}{n-1}}. \quad . . . . . (42)$$



These two relations, according to the new hypothesis, take the place of equations (35) and (36), and now, for the case that  $p_2:p_1$  is smaller than the value  $x_m$  given by equation (41), there follows, from (33) and (34),

$$w = \sqrt{\frac{2g\kappa}{\kappa+1}} p_1 v_1, \quad . \quad . \quad . \quad . \quad . \quad (43)$$

$$\frac{G_m}{F} = \left( \frac{2}{\kappa+1} \right)^{\frac{1}{n-1}} \sqrt{\frac{2g\kappa}{\kappa+1}} \frac{p_1}{v_1}, \quad . \quad . \quad . \quad . \quad (44)$$

If, for abbreviation, we use

$$\phi = \left( \frac{2}{\kappa+1} \right)^{\frac{1}{n-1}} \sqrt{2g \frac{\kappa}{\kappa+1}}, \quad . \quad . \quad . \quad . \quad . \quad (45)$$

we get

$$\frac{G_m}{F} = \phi \frac{p_1}{v_1}, \quad . \quad . \quad . \quad . \quad . \quad (45a)$$

In accordance with the preceding formulas, the following table was calculated for a series of different values of the efflux exponent  $n$ .

$n$	$\frac{p}{p_1}$	$\frac{v}{v_1}$	$\phi$
1.10	0.1286	6.4547	0.5249
1.15	0.2394	3.4667	0.9773
1.20	0.3266	2.5466	1.3336
1.25	0.3936	2.1084	1.6069
1.30	0.4457	1.8619	1.8197
1.35	0.4871	1.7037	1.9887
1.41	0.5266	1.5759	2.1499

The greater the resistances, the smaller the corresponding value of  $n$ ; accordingly the smaller also is the pressure  $p$  which settles in the orifice. For simple orifices, to which we must add the frequently occurring conical and converging nozzles, only the values in the four last rows of the preceding table need be considered. If air is allowed to pass from the free atmospheric space, through a simple orifice, into a large, closed, vessel, originally a

vacuum, then, in every unit of time, there will flow into it always the same quantity of air, the quantity which is determined by equation (45a), and the velocity of influx will be invariable and equal to the acoustic velocity of equation (43). As soon as the pressure  $p_2$  in the vessel has reached the value  $p$  prescribed by equation (41) the conditions change; from there on the influx velocity  $w$ , and the quantity of air  $G$ , entering in a unit of time, must be estimated by equations (33) and (34); in so doing the value  $G:F$  gradually diminishes.

**Example 1.** Let us suppose air to flow from a large vessel in which the pressure is 1.5 atmospheres and the temperature  $15^\circ \text{C}$ . [ $59^\circ \text{F}$ .] and that it flows under constant pressure into the free atmosphere where the pressure  $p_2$  = one atmosphere (10333 kg. per square meter) [2116.31 pounds per square foot] prevails. Let the efflux take place through a well-rounded orifice for which experiment has given an efflux exponent  $n = 1.375$ .

Here we get, first of all, according to equation (41),

$$\frac{p}{p_1} = \left( \frac{2}{\kappa + 1} \right)^{\frac{n}{n-1}} = 0.5047;$$

hence  $p = 0.7570$  atmospheres, so that  $p_2 > p$ . In this case the external pressure  $p_2$  extends up to the plane of the orifice, and therefore we must use equations (33) and (34) with

$$\frac{p}{p_1} = \frac{p_2}{p_1} = \frac{2}{3}.$$

Because  $T_1 = 288^\circ \text{C}$ . ( $518.4^\circ \text{F}$ .) we get, from  $p_1 v_1 = B T_1$  with  $B = 29.269$  [ $B = 53.349$ ], for the specific volume of the air in the discharging vessel  $v_1 = 0.5438$  cbm. [8.7068 cu. ft.].

Now from

$$\left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} = \frac{T}{T_1} = 0.8953$$

there follows for the temperature  $T$  in the orifice,  $257.8^\circ$  or  $-15.2^\circ \text{C}$ . [ $464.04^\circ$  or  $4.64^\circ \text{F}$ .].

The specific volume  $v$  in the orifice is computed from

$$\frac{v}{v_1} = \left( \frac{p_1}{p_2} \right)^{\frac{1}{n}} = 1.3430,$$

and from it we find

$$v = 0.7303 \text{ cbm.}$$

$$[v = 11.693 \text{ cu. ft.}]$$

Equation (33) gives for the efflux velocity

$$w = 244.03 \text{ m.}$$

$$[w = 800.63 \text{ ft.}],$$

and from  $Gv = Fw$  there follows directly

$$\frac{G}{F} = \frac{w}{v} = 334.15 \text{ kg. [68.45 lb.],}$$

when the orifice of efflux  $F$  is measured in square meters [square feet].

The latter value can also be written

$$\frac{G}{F} = 1.9793 \sqrt{\frac{p_1}{v_1}}$$

$$\left[ \frac{G}{F} = 3.5851 \sqrt{\frac{p_1}{v_1}} \right].$$

The discharge in cubic meters per second, measured under the inner pressure, is

$$Gv_1 = 181.7 F$$

$$[Gv_1 = 596.3 F];$$

on the other hand, measured in the plane of the orifice,

$$Gv = 244.0 F$$

$$[Gv = 800.53 F].$$

After the jet has spread itself outside, the air again has the initial temperature of  $15^\circ \text{ C. [} 59^\circ \text{ F.]}$  and the specific volume  $v_2$  is found from the relation

$$p_2 v_2 = p_1 v_1 \text{ or } v_2 = 0.8157 [13.067 \text{ cu. ft.}].$$

Accordingly, the air discharged per second, measured under the outer pressure, is

$$Gv_2 = 272.6 F$$

$$[Gv_2 = 894.37 F].$$

The energy of flow in the plane of the orifice is

$$\frac{w^2}{2g} = 3035.2 \text{ mkg. [9958.1 ft-lb.],}$$

and because the coefficient of resistance  $\zeta$ , according to equation (32), is

$$\zeta = 0.066,$$

the loss of energy, in consequence of the resistances, is

$$\zeta \frac{w^2}{2g} = 200.2 \text{ mkg. } [657.23^* \text{ ft-lb.}]$$

**E x a m p l e 2.** Suppose that in a large vessel there is air of four atmospheres pressure, at a temperature of  $15^\circ \text{ C. } [59^\circ \text{ F.}]$ . Then by the equation of condition  $p_1 = 4 \times 10333$ , and  $T_1 = 273 + 15^\circ [518.4]$ , the specific volume there is  $v_1 = 0.2039 \text{ cbm. } [3.266 \text{ cu. ft.}]$ . If this air flows, under constant pressure, through a well-rounded orifice, for which we again assume the efflux exponent  $n = 1.375$ , into the free atmosphere, so that  $p_2$  corresponds to the pressure of one atmosphere, then again, as in the preceding example, we get from equation (41)

$$\frac{p}{p_1} = 0.5047.$$

Hence the pressure in the orifice is  $p = 2.0188$  atmospheres, and therefore  $p_2 < p$ , so that  $p$  here represents the real pressure in the orifice, and to be calculated requires equations (43) and (44); first of all, from equation (42) we compute

$$\frac{v}{v_1} = 1.6442,$$

that is,

$$v = 0.3352 [5.3695 \text{ cu. ft.}],$$

and then get

$$w = 311.06 \text{ m. } [1020.54 \text{ ft.}] \text{ (acoustic velocity);}$$

also

$$\frac{G}{F} = 2.0646 \sqrt{\frac{p_1}{v_1}} = 927.6 \text{ kg. } [190.0 \text{ lb.}],$$

which last value will hold even for flow into a vacuum.

Moreover

$$\frac{T}{T_1} = \frac{2}{\kappa + 1} = 0.8298,$$

hence the temperature in the plane of the orifice is  $T = 239^\circ$  or  $-34^\circ \text{ C. } [T = 430.2 \text{ or } -29.2 \text{ F.}]$ .

### § 45. EFFLUX UNDER CONSTANT PRESSURE WITH SMALL DIFFERENCES OF PRESSURE.

If the pressure  $p_1$  in the discharging vessel is but little larger than the external pressure  $p_2$ , it must be taken as identical with pressure  $p$  in the plane of the orifice, and then equation (33) gives for the energy of flow in the orifice

$$H = \frac{w^2}{2g} = \frac{\kappa}{\kappa-1} p_1 v_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \right].$$

But for small differences of pressure  $p_1 - p_2$

$$\left( \frac{p_2}{p_1} \right)^{\frac{n-1}{n}} = \left( 1 - \frac{p_1 - p_2}{p_1} \right)^{\frac{n-1}{n}} = 1 - \left( \frac{n-1}{n} \right) \left( \frac{p_1 - p_2}{p_1} \right).$$

Substitution in the preceding equation therefore gives the velocity of efflux

$$w = \sqrt{2g \frac{\kappa(n-1)}{n(\kappa-1)}} v_1 (p_1 - p_2). \quad . \quad . \quad . \quad (46)$$

If we here also introduce the coefficient of resistance  $\zeta$  as per equation (32), which furnishes

$$1 + \zeta = \frac{n(\kappa-1)}{\kappa(n-1)},$$

we have

$$w = \sqrt{2g \frac{v_1(p_1 - p_2)}{1 + \zeta}}, \quad . \quad . \quad . \quad . \quad (46a)$$

and this formula agrees completely with that one which was derived and used in practical Hydraulics for the efflux of liquids (water). The same formula is found directly from equation (IIIb), if we there substitute the work of resistance  $W = \zeta H$  and integrate the equation under the supposition that the specific volume of the air is constant during the flow toward the orifice,

so that we may write  $v=v_1$ . Under this hypothesis, and neglecting the work of resistance, equation (46a) was derived from equation (IIIb) by Daniel and John Bernoulli, Euler, d'Alembert, and then utilized in the investigations of technical Mechanics by Poncelet. But it was Weisbach who in his *Ingenieur- und Maschinenmechanik* first made extensive use of equation (46a), exactly in the form here given. The equation is, in fact, of great technical importance, because in blowers, fans, air, in the motion of atmospheric air and of illuminating gas in pipes, etc., there are always slight differences of pressure. In all related investigations, when considering the different kinds of resistances, for example, curves, elbows, and sudden enlargements in pipes, we can, as suggested by Weisbach, employ the same coefficients of resistance as are employed under like circumstances for the motion of water. As regards the quantity of air  $G$ , we find for it, from the relation  $Gv=Fw$ , with the help of equation (46a),

$$G=F\sqrt{\frac{2g}{1+\zeta} \frac{r_1}{v} \frac{(p_1-p_2)}{v}}. \quad . \quad . \quad . \quad . \quad (47)$$

As  $v$  is nearly identical with  $v_1$ , and because the temperature in the plane of the orifice is nearly the same as that in the discharging vessel, so that we can assume the relation  $p_2v=BT_1$ , we can approximately find the discharge:

$$G=F\sqrt{\frac{2g}{1+\zeta} \frac{p_2(p_1-p_2)}{BT_1}}, \quad . \quad . \quad . \quad . \quad (47a)$$

an equation which agrees in form with that given by Napier for the efflux of steam under slight excess of pressure; we will return later to Napier's investigations. The assumption that the specific volume is constant really presupposes the withdrawal of heat, namely, from equation (Ib), p. 232, there follows immediately, by integration, for  $v=v_1$ ,

$$Q=AH-\frac{A\kappa}{\kappa-1}r_1(p_1-p),$$

and if we determine the flow of energy

$$H = \frac{w^2}{2g}$$

from equation (46), and substitute it, there results the quantity of heat  $Q$  which, as the negative sign shows, must be withdrawn from the unit of weight of air during the flow toward the orifice:

$$Q = - \frac{A\kappa}{n(\kappa-1)} v_1(p_1-p).$$

Alongside of equation (46a), which is valid for slight differences of pressure, there is also given in mechanical and physical writings one other efflux formula, which was first developed by N a v i e r, and is commonly said to hold also for the greater differences of pressure.

If we assume that the temperature  $T$  of the gas in the orifice can be taken as identical with that ( $T_1$ ) in the discharging vessel, there follows  $pv = p_1v_1$ , and hence from equation (IIIb), when we again replace the work of resistance  $W$  by  $\zeta H$ , we get

$$w = \sqrt{\frac{2g}{1+\zeta} p_1 v_1 \log_e \frac{p_1}{p}}, \quad . \quad . \quad . \quad . \quad . \quad (48)$$

and the discharge, disregarding contraction,

$$G = \frac{Fw}{v} = F \sqrt{\frac{2g}{1+\zeta} \frac{p_1}{v_1} \left(\frac{p}{p_1}\right)^2 \log_e \frac{p_1}{p}}, \quad . \quad . \quad . \quad (49)$$

which equation can be brought, with the help of the relation  $pv = p_1v_1 = BT_1$ , into other forms. Equation (48), as was mentioned, is found in all the manuals on Physics, and yet it is derived from assumptions which, for several reasons, must be regarded as not at all permissible.

If we assume first that the external pressure  $p_2$  extends to the plane of the orifice, and designate the ratio  $p:p_1$  by  $x$ , then equa-

tion (49) shows that for a particular inner pressure  $p_1$  there is a value of  $x$  for which the discharge  $G$  becomes a maximum; this occurs with the maximum value of the expression

$$x^2 \log_e \frac{1}{x},$$

and for

$$\log_e \frac{1}{x} = \frac{1}{2}$$

acquires the value

$$\frac{p_2}{p_1} = 0.6055 \quad \text{or} \quad \frac{p_1}{p_2} = 1.687.$$

Accordingly if the inner pressure amounts to more than, say, 1.65 of the external pressure, formula (49) will then become useless and we must have recourse to an hypothesis like or similar to the one discussed above. Although the preceding proof was given by Coriolis<sup>1</sup> (1838), nevertheless Navier's formula was presented as suitable for the greater differences of pressure. We must also note that under the assumption  $pv = p_1v_1$  equation (Ib) gives

$$Q = AH;$$

therefore, in order that the hypothesis may be realized, the unit of weight of gas must receive, while flowing toward the orifice, a quantity of heat corresponding to the full energy of flow in the plane of the orifice, a case which never occurs in ordinary efflux.

#### § 46. EXPERIMENTS ON THE EFFLUX OF AIR THROUGH SIMPLE ORIFICES.

The older experiments of Schmidt, Lagerhjelm, Koch, and d'Aubuisson (1820 to 1826), already mentioned on p. 239), were all conducted with very small excess of pressure and in such a way that the air-filled discharging vessel was in communication with a vessel of water, from which the water flowed into the former vessel with a certain excess of pressure. The volume of the entering water gives the volume of the

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<sup>1</sup> Comptes rendus, 1838, VI, p. 239; also 1839, VIII, p. 295.



air (measured at the inner pressure) which at the same time is displaced and is then discharged through the orifice. As was mentioned, all these experiments were conducted with a very slight excess of pressure and also with very small orifice diameters, in fact, on a small scale; <sup>1</sup> they furnish, as was shown later by Buff,<sup>2</sup> with the help of his own experiments, the proof that for the efflux of air there can be employed the same formulas and the same coefficients of efflux as for the efflux of water. But for greater excess of pressure the propositions in question are not directly available; these experiments, particularly, do not give any clue whatever as to the orifice pressure discussed above.

The first experiments, on a larger scale and with a larger excess of pressure, are due to Weisbach, as repeatedly mentioned above; very valuable as these experimental results are in general, nevertheless they are not suited to decide the question concerning the pressure in the orifice, because Weisbach's pressures in the discharging vessel were too small; in only a few of his experiments did the initial pressure of the air in the boiler somewhat exceed two atmospheres, i.e., at most, it was double the external pressure. In the experiments of de Saint-Venant and Wanzel the ratio of the pressure in the discharging vessel to that in the receiving vessel was, to be sure, far greater than two; they allowed air to flow into the receiver of an air-pump through orifices of only  $\frac{2}{3}$ , 1, and 1.5 mm. [0.026, 0.039, 0.059 in.], the receiver having a capacity of 0.0174 cbm. [0.6145 cu. ft.], in which the pressure at the beginning of the different series of experiments was generally from 10 to 20 mm. of mercury [0.4 to 0.8 in.]. They employed two methods. In the first they allowed the external air to flow in without interruption till the pressure in the receiver equaled the external pressure and observed at equal intervals of time (every 5 seconds) the increment of pressure; in the second method, which alone could have realized

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<sup>1</sup> Weisbach reports the older experiments on the efflux of air and, at the same time, gives full references to the literature, in "Allgemeine Maschinen-Encyklopädie," article "Ausfluss," p. 603.

<sup>2</sup> Buff, "Versuche über den Widerstand ausströmender Luft," Poggendorff's Annalen, Vol. 40, 1837, p. 14.

their aim, they allowed the air to flow in with interruptions; after every efflux, of 5 seconds' duration, the orifice was closed with the finger for a few seconds and the pressure quickly noted. The defective feature of this method is that the experimenter did not keep the orifice closed long enough, and after closing it, did not wait for the (diminishing) manometer reading of the receiver to become stationary. If we add to this the fact, criticized by Poncelet, that the diameters of the orifices used and the capacity of the receiver were much too small,<sup>1</sup> then it seems justifiable to institute new experiments on a larger scale, with high boiler pressure and with more reliable experimental methods.

Now I first made such experiments in Zürich in 1871 (see p. 193). The mechanical section of its Polytechnicum already possessed at that time a series of experimental machines and apparatus, and, in a modest way, followed the same aims now pursued in the mechanical engineering laboratories of technical high schools. I had especially constructed, for the contemplated experiments on the efflux of air, a wrought-iron, cylindrical boiler 4.2 m. [13.776 ft.] long and 0.5 m. [1.64 ft.] in diameter, whose cubic capacity, carefully calibrated with water, gave 0.81088 cbm. [28.637 cu. ft.]. The boiler was tested up to ten atmospheres, and was provided with a pump by means of which external atmospheric air was compressed and forced into the boiler; the pump-piston was driven by a crank worked by hand, so that naturally the filling of the boiler with air, of the usual four atmospheres of pressure, took a long time.

The boiler carried a dome<sup>2</sup> provided with large pipe connec-

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<sup>1</sup> de Saint Venant and Wantzel replied to Poncelet's objections (*Comptes rendus*, 1845, XXI, p. 195) in the same volume, p. 366, whereupon Poncelet retorted somewhat violently, designating the experiments as "so to speak, microscopic," and characterized as unusual and odd the law of constancy of discharge with an external pressure which was smaller than about one-half the inner one. In the latter respect Poncelet did the experimenters mentioned decided injustice, as my experiments, given in the text, show.

<sup>2</sup> The boiler dome mentioned in the text is illustrated in *Der Civilingenieur* (1874), Vol. 20, Plate 1.

tions all of which were closed except the one used in the efflux experiments; this pipe was provided with a tight-fitting cock whose passageway had the same inner diameter as the pipe. In the plane of the open end of the latter, various orifices were inserted. A carefully graduated, open, manometer was connected with the interior of the boiler, and from it could be read off pressures up to four atmospheres (three atmospheres gauge pressure). Experiments were conducted with three kinds of simple orifices well rounded on the inside and with short, cylindrical adjutages without interior rounding, and with orifices in a thin wall.

After the boiler was filled with air of about four atmospheres, and after equalization with the external atmosphere had taken place so that the manometer was stationary, the cock (with a quarter turn) was quickly opened and, after about ten seconds, was quickly closed and the manometer reading noted; in so doing the pressure  $p_1$  was read before the opening,  $p_x$  immediately after the closing,  $p_y$  immediately afterward (after the jump—see remarks on p. 193), and, finally,  $p_2$  was read, namely, as soon as the manometer reading again showed itself stationary (because of the equalization of temperature) after the closing of the orifice; this equalization usually occurred after ten to fifteen minutes. Now the experiment was repeated with the pressure  $p_2$  as the new initial pressure  $p_1$ , and this was continued till the boiler pressure had nearly fallen to the external atmospheric pressure. Thus there resulted for one filling of the boiler and for one and the same orifice a whole series of separate experiments, whose number was of course greater the smaller the diameter of the orifice used.

From each individual experiment there was found, from the volume of the boiler, from the temperature, from the pressure  $p_1$  at the beginning and from the pressure  $p_2$  at the end, after equalization of temperature, the weight of air in the boiler at the beginning and at the end, and then, from the observed time of efflux, the discharge per second was determined.

The most exact possible determination of this period of efflux is of importance in this experimental method, efflux during short intervals. For this purpose a clock was used which kept fifths

of a second and in which the moving index noted, on the dial immediately below the scale of seconds, a colored point, as soon as a button on the clock casing was pressed. The pressing of the button was effected by an electromagnet; to the cock of the efflux pipe there was fastened a metallic pointer which, at the middle position of the cock, dipped a little into the mercury that was in a vessel to one side of the cock; the dipping, during the turning of the cock, closed the metallic circuit and operated the magnet. In this way, at the instant of operating the cock and at the instant of closing the cock, there was put on the dial-plate of the clock a point whose position opposite the scale of seconds enabled one to read with great ease the duration. The experimental results also showed that this method of determining the period of efflux was completely accurate within 0.2 of a second; any uncertainties were neutralized by the great number of separate experiments from which could be found, finally reliable, mean values of the quantities to be determined.

The experiments themselves dissipated also my original doubt whether or no, with the short efflux period employed, the time which had elapsed till the efflux had attained its normal state might not be relatively too large; I convinced myself that with the size of the boiler and the orifice areas employed, this period must be almost infinitesimal, and inferred this from the peculiar tone of the violent noise which was connected with the efflux of the compressed air; this tone was clap-like at the instant of opening the cock and was maintained at the same pitch during the short period of efflux; with a long period of efflux this tone changed slowly and continuously, and here, in a certain sense, one could follow with the ear a gradual diminution of pressure in the boiler.

A preliminary report of these experiments was made public in 1874 in *Der Civilingenieur*,<sup>1</sup> after a lecture which I delivered in 1871 to the Saxon Society of Engineers in Leipsic. Later, with the same efflux apparatus, *Fliegner* again took up the experiments<sup>2</sup> with short orifices and added to my experiments the

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<sup>1</sup> "Resultate experimenteller Untersuchungen über das Ausströmen der Luft bei starkem Überdruck," *Civilingenieur*, 1874, Vol. 20, p. 1.

<sup>2</sup> *Fliegner*, *Ergebnisse einiger Versuche über das Ausströmen der atmosphärischen Luft*," *Civilingenieur*, 1874, Vol. 20, p. 13.

results of his own. Where I found for such orifices the efflux exponent  $n=1.403$ , *Fliegner* concludes that  $n=\kappa=1.410$ , so that here, in the main, the influence of the resistances could be neglected. The same conclusion is reached by *Emil Herrmann* in a discussion of our experiments ("Compendium der mechanischen Wärmetheorie," Berlin, 1879).

By a further study of the problem *Fliegner* was led to new experiments which gave, for the kind of orifice mentioned,  $n=1.37$ , after certain changes and improvements had been made in the experimental apparatus used.<sup>1</sup>

I reported, as completely as the space permitted, in an earlier edition of this book (Vol. 1, 1887), on the results of my numerous experiments made in 1871 with different simple orifices, and therefore will not here return to them. The experiments were, to be sure, sufficiently reliable and realized what was their main purpose, namely, to thoroughly confirm the proposition of *de Saint-Venant* and *Wantzel* about the orifice pressure, whose correctness was doubted by *Poncelet*; but the experimental method showed certain defects which rendered impossible a perfectly reliable determination of the resistances during efflux; on the whole, it does not seem suitable to compress the air in the discharging vessel by pumps and allow it to flow into the free atmosphere. With simple orifices, as was repeatedly emphasized above, the inner pressure  $p$  should be at least double the outside pressure  $p_2$ ; but we recognize from the formula given above that the controlling element is not the pressure difference  $p_1-p_2$ , but the pressure ratio  $p_1:p_2$ ; the latter ratio was at most  $\frac{p_1}{p_2}=4$  in the experiments, and while this lasted the pressure  $p_1$  diminished and  $p_2$  (the external atmospheric pressure) remained constant during the period of observation. Although the internal pressure  $p_1$  could be taken higher, by using thicker boiler-plate, this would not remove another greater defect. To be sure one can determine the pressure and temperature shown in the discharging

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<sup>1</sup> *Fliegner*, "Versuche über das Ausströmen der atmosphärischen Luft durch gut abgerundete Mündungen," *Civilingenieur*, 1877, Vol. 23, p. 443.

vessel with great accuracy in the condition of equilibrium, but cannot determine the degree of moisture in the air, and, besides, the air was also rendered somewhat impure by the lubricants used for the pistons of the force-pump (i.e., by the oil vapors).

I have cherished for years the desire to again take up the experiments in another way, moreover, theoretical studies of the motion of air in long pipes (with great resistances) showed that the experiments on efflux into the free atmosphere could only lead to the goal when very high pressures were employed in the discharging vessel, that is, with very large values of the ratio  $p_1 : p_2$ .

I therefore in 1897 conducted new experiments, by going back to the experimental method of de Saint-Venant and W a n t z e l (see p. 258 above), but carried out the experiments on a considerably larger scale with the means of recent times at my disposal.

I allowed the outer atmospheric air to stream into a large boiler in which the air could be kept in a highly rarefied condition by an excellently made air pump, driven by a S c h m i d t water motor. The advantages of this experimental method are at once apparent: the external space, the free atmosphere, constitutes the discharging vessel in which the pressure remains absolutely constant during the flow and in which the state of the air with respect to moisture can be accurately determined. The pressure of the air in the receiving vessel (the boiler) can easily be brought to  $p_2 = 25$  mm. [1 in.] of mercury; with a total barometric pressure of  $p_1 = 750$  mm. [30 in.] we should have therefore at the beginning of the experiment  $p_1 : p_2 = 30$ , just as if air of 30 atmospheres pressure flowed into the free atmosphere, and then the difference of pressure would still be only  $p_1 - p_2 = 715$  mm. [29 in.], or about 0.95 of an atmosphere; experiments with long pipes are thus also rendered possible.

### § 47. NEW EXPERIMENTS ON THE EFFLUX OF AIR THROUGH WELL-ROUNDED ORIFICES.

In the Mechanical Engineering Laboratory II (for prime movers) at the Royal Technical High School in Dresden there were set up, at my suggestion, two upright boilers each 1.3 m. [4.265 ft.] in diameter and 3.4 m. [11.155 ft.] in height (measured at the middle of the dished ends), and possessing a capacity of about 4.2 cbm.<sup>1</sup> [148.33 cu. ft.]. The boilers were tested up to 15 kg/qcm. [213.35 lb. per sq. in.] gauge pressure and were joined by a connecting pipe which was closed air-tight by a cock when only one boiler was employed. With the outfit it was possible to conduct the most varied pneumatic experiments; I will here briefly discuss the first experiments of this sort, which I made in April, 1897, with well-rounded orifices, but will first preface the discussion by some remarks on ordinary atmospheric air.

Let  $T_1$  be the temperature and  $b_1$  the barometric reading in millimeters [inches] of mercury. Then the corresponding specific pressure will be  $p_1 = 13.596 b_1$  [ $p_1 = 70.73 b_1$ ]. Now air consists of a mixture of dry atmospheric air and of the vapor of water whose pressure is here always so small that we may assume that the vapor follows exactly the law of Mariotte and Gay-Lussac; now in the equation of condition for gases,  $pv = BT$ , the constant for dry air is  $B = 29.269$  [ $B = 53.349$ ] (see p. 104), and for steam it is  $B = 46.954$  [85.584] (see p. 114); the ratio of the first value to the second, which we will designate by  $\epsilon$ , represents the relative weight of steam to air, and is  $\epsilon = 0.623$ . If we retain the letter  $B$  for the gas constant of dry air, then the constant for steam is  $\frac{B}{\epsilon}$ .

Now let  $p'$  be the pressure of the dry air in the mixture,  $\gamma'$  its specific weight (weight per cubic unit), and let  $p''$  be the pressure

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<sup>1</sup> A cut of the boilers, taken from a photograph, is shown in the *Zeitschrift für Architektur und Ingenieurwesen*, 1898, Vol. 46, p. 549, and accompanies an article by Ernst Lewicki: "Das Laboratorium für Kraftmaschinen an der K. S. Technischen Hochschule zu Dresden."

of the steam present (called vapor-pressure), and let  $\gamma''$  be its specific weight, then we have the relations

$$\frac{p'}{\gamma'} = BT_1 \quad \text{and} \quad \frac{p''}{\gamma''} = \frac{BT_1}{\epsilon},$$

and the total air pressure  $p_1$  is

$$p_1 = p' + p'',$$

and the specific weight  $\gamma_1$  of the mixture

$$\gamma_1 = \gamma' + \gamma''.$$

A combination of the equations gives

$$\gamma_1 = \frac{p_1 - (1 - \epsilon)p''}{BT_1}.$$

Now let us put

$$\frac{p_1}{\gamma_1} = B_m T_1,$$

where  $B_m$  represents the gas constant for the mixture, that is, for the (moist) air actually present, which is equal to

$$B_m = \frac{B}{1 - (1 - \epsilon) \frac{p''}{p_1}}. \quad . \quad . \quad . \quad . \quad . \quad (51)$$

We see from these formulas that the specific weight of moist air is smaller, and the gas constant larger, than for dry air. As was mentioned, the pressure  $p_1$  and the temperature  $T_1$  of the mixture are regarded as known; on the other hand the vapor-pressure  $p''$  is still to be determined. For this purpose *Lambrecht's* "dew-point mirror" is used, and by a gradual cooling of the air it is found at what temperature (dew-point) steam begins to condense on a smooth mirror surface. If  $T_0$  is the temperature in question we can find from the steam tables for saturated vapor the corresponding steam pressure, which we will designate by  $p_0$ .

Then the relation holds

$$\frac{p_0}{\gamma''} = \frac{BT_0}{\epsilon},$$



which, combined with the above equation for  $p'' : \gamma''$ , will enable us to compute the vapor-pressure,

$$p'' = \frac{T_1}{T_0} p_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

and then will enable us to calculate the constant  $B_m$  according to equation (51).

From the formula

$$p_1 v_1 = \frac{p_1}{\gamma_1} = B_m T_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

there is finally determined the specific volume  $v_1$  and the specific weight  $\gamma_1$  of the moist air.

If we suppose the air to be completely saturated with vapor, and that  $p_0''$  is the vapor-pressure which corresponds to the temperature  $T_1$  (taken from the steam tables), and  $\gamma_0''$  the specific weight of the steam, then we have the relation

$$\frac{p_0''}{\gamma_0''} = \frac{B T_1}{\varepsilon},$$

and from the above equation for  $p'' : \gamma''$  there follows

$$\frac{\gamma''}{\gamma_0''} = \frac{p''}{p_0''} = x, \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

where  $x$  now represents the "moisture" of the air in the form in which it is ordinarily presented in Meteorology.

In the flow experiments themselves only one of the two boilers was employed, its capacity having been first determined by most careful calibration with water and fixed at  $V = 4.2270$  cbm. [149.28 cu. ft.]. The boiler was provided with a good, mercury, vacuum gauge whose reading in millimeters of mercury was subtracted from the barometer reading  $b_1$  in order to get the pressure of the air in the boiler in millimeters of mercury. When the reading of the vacuum gauge was stationary it was taken as proof that the temperature of the air in the boiler agreed with the external temperature of the air.

In the boiler shell there was an opening into which was inserted the orifice for the influx of air; ordinarily the orifice is closed on the

outside by a plate (clack) which is made air-tight by being pressed with strong springs. By a cleverly designed closing mechanism the spring is released by a simple pull and the clack jumps back and can in a similar way be brought back to the original position by spring force. During the opening as well as the closing of the clack there is marked, by electrical means, on the dial plate of the clock mentioned (p. 261) exactly the instant of time, so that we can read the period during which the opening exists, and consequently the flow of air occurs, with an accuracy which is correct down to 0.1 to 0.2 of a second.

The experiments were then conducted in the following manner.

After inserting the orifice and rendering it air-tight with respect to the outside, the boiler was pumped out till it was nearly in the condition of a vacuum, and after the pressure  $b_2$  became stationary it was read from the vacuum gauge. Then I allowed the air to flow for  $t$  seconds, and at the end observed the pressure  $b_3$  after the equalization of temperature. Thereupon the experiment was repeated with the pressure  $p_3$  as initial pressure and the end pressure determined, etc. In this way there resulted a series of separate observations for each of which the value

$$\frac{b_3 - b_2}{t} = \phi$$

had to be computed. The determination of this quantity was the purpose of the observation.

Let  $p$  be the specific pressure in the vessel,  $T_1$  the temperature there, and  $\gamma$  the specific weight,  $V$  the boiler capacity, and  $G_k$  the weight of air filling the boiler, then

$$G_k = V\gamma = \frac{Vp}{B_m T_1}.$$

If the composition of the air in the boiler is like that outside, we must put  $p_1$  in place of  $p$ ; on the other hand, if  $p_2$  is the pressure at the beginning and  $p_3$  the pressure at the end of some one experiment, then the quantity of air which has entered in  $t$  seconds is

$$G_t = V\gamma_1 \frac{p_3 - p_2}{p_1},$$

and consequently the weight of air  $G$  per second is

$$G = \frac{V\gamma_1}{b_1} \frac{b_3 - b_2}{t},$$

where  $\gamma_1$  refers to the outer air and  $b$  represents the pressures in millimeters [inches] of mercury. If  $F$  is the cross-section of the orifice in square meters [square feet] we get, for every separate experiment, the quantity of air per second in kilograms per sq. m. [lb. per sq. ft.], as follows:

$$\frac{G}{F} = \frac{V\gamma_1}{Fb_1} \frac{b_3 - b_2}{t} \dots \dots \dots (55)$$

Of the different experiments conducted with well-rounded orifices we will here adduce a series for an orifice of 5.1 mm. [0.2008 in.] diameter.

#### Well-rounded Orifices.

Diameter  $d=5.1$  mm. [0.20079 in.], cross-section  $F=20.428 \times 10^{-6}$  sq. m. [0.03166 sq. in.], barometer reading  $b_1=754$  mm. [29.655 in.], temperature of air  $T_1=273+15.8=288.8^\circ$  [519.84°], dew point  $T_v=273+9.6=282.6^\circ$  [508.68°], and corresponding pressure of vapor  $b_0=8.93$  mm. [0.3516 in.].

No.	Duration of Flow $t''$	Equi- librium pressure $b_2$ $b_3$	Values of $\frac{b_3 - b_2}{t} = \phi$	No.	Duration of Flow $t''$	Equi- librium pressure $b_2$ $b_3$	Values of $\frac{b_3 - b_2}{t} = \phi$
First Part.				Second Part.			
1	46.8	27.8	0.6902	10	66.6	413.3	0.6802
2	48.5	60.1	0.6969	11	63.9	458.6	0.6651
3	64.1	93.9	0.6928	12	67.2	501.1	0.6399
4	67.4	138.3	0.6914	13	68.4	544.1	0.5994
5	66.9	184.9	0.6936	14	110.8	585.1	0.5334
6	65.2	231.3	0.6887	15	126.6	644.2	0.4218
7	67.0	276.2	0.6896			697.6	
8	65.3	322.4	0.6922				
9	66.2	367.6	0.6903				
		413.3					

Mean value  $\phi=0.6917$  [0.02723]

For the given temperature of the air and of the dew point we have, according to equation (52), the vapor-pressure  $b'' = 9.12$  mm. [0.3591 in.], and, according to equation (51), the gas constant for outer atmospheric air

$$B_m = 29.403 [53.593],$$

therefore according to equation (53) for its specific weight and its specific volume we have

$$\begin{aligned} \gamma_1 &= 1.2072 \text{ kg.}, & v_1 &= 0.8283 \text{ cbm.} \\ [\gamma_1 &= 0.075366 \text{ lb.}, & v_1 &= 13.269 \text{ cu. ft.}] \end{aligned}$$

For the temperature of air given we have the saturation pressure  $b_0'' = 13.37$  mm. [0.5264 in.] of the vapor of water, and consequently, according to equation (54), the moisture of the air is  $x = 0.696$ .

According to these investigations, the quantity of air passing through the orifice in a second must always be the same so long as the pressure in the boiler is about half of the external pressure, that is, smaller than 377 mm. [14.843 in.]. The value of  $\phi$  in the first rows of the preceding table confirms this completely, for they seem to be constant and scarcely deviate from the mean value; according to equation (55),  $G$  is simply proportional to the value of  $\phi$ . In the second part of the experiments in which the inner pressure was greater, the values of  $\phi$  diminish decidedly with the growing pressure.

With the given values and the mean value  $\phi$ , equation (55) gives for the first part of the experiment

$$\frac{G}{F} = 331.29 \frac{b_3 - b_2}{t} = 229.1 \text{ kg. [46.923 lb.]}$$

As we here calculate for the external atmospheric air

$$\sqrt{\frac{p_1}{v_1}} = 111.23 [= 12.577],$$

we can also write

$$\begin{aligned} \frac{G}{F} &= 2.0602 \sqrt{\frac{p_1}{v_1}}. \\ \left[ \frac{G}{F} &= 3.7317 \sqrt{\frac{p_1}{v_1}} \right]. \end{aligned}$$

We compute  $\psi$  from

$$\left(\frac{2}{\kappa+1}\right)^{\frac{1}{n-1}} \sqrt{\frac{2g}{\kappa+1}} = \psi$$

and find it to be  $\psi=2.0602$  [3.7317], and then equations (45) and (45a) give, for the efflux exponent  $n$ , the value

$$n=1.375.$$

For another series of experiments with an orifice diameter of  $d=10.85$  mm. [0.4272 in.] there was found

$$\begin{aligned} \frac{G}{F} &= 228.2, \quad \psi = 2.0594, \quad \text{and} \quad n = 1.374 \\ \left[ \frac{G}{F} &= 46.63, \quad \psi = 3.7302 \right]; \end{aligned}$$

in the third series of experiments with an orifice diameter of  $d=15.15$  mm. [0.5965 in.] there was found

$$\begin{aligned} \frac{G}{F} &= 230.4, \quad \psi = 2.0785, \quad \text{and} \quad n = 1.386 \\ \left[ \frac{G}{F} &= 47.18, \quad \psi = 3.7648 \right]. \end{aligned}$$

According to equation (32) the three values of  $n$  correspond to the coefficient resistances  $\zeta=0.066$ , 0.068, and 0.044, which values lie within the limits also found for the efflux of water.

The result therefore follows that in the efflux of air through simple orifices we can use the coefficient of resistance for water, not only for small differences of pressure, but also with the largest efflux velocities, when it is a question of determining the quantities discharged.

In the above-given efflux experiments there were observed for each separate experiment not only the initial and final pressures (in the state of equilibrium), but also the instantaneous pressure  $b_x$  at the moment of closing the orifice, and the pressure  $b_y$  after the close of the orifice (after the jump); the values were not tabulated because it has no significance for the problem before us. Thus, for the examples in experiment 1 of the above tabula-

tion, there was found  $b_2=27.8$  mm. [1.112 in.],  $b_x=61.4$  [2.456],  $b_y=60.3$  [2.412],  $b_3=60.1$  mm. [2.404 in.] of mercury. The time needed for the final equalization of pressure amounted to about ten minutes. As regards the jump of the pressure there appeared here also the phenomenon which had already been observed by de Saint Venant and Wantzel (see p. 194). During efflux into the boiler the temperature of the air there rises (on account of the compression of the air); consequently, during the equalization of pressure, heat is withdrawn through the boiler walls and given to the outside. The exchange of heat between the air and walls appears to be particularly vigorous immediately after the closing of the orifice, when the stormy air of the interior comes into contact with the walls.

Very remarkable was the observation that the flow of air into the boiler took place with perfect quiet during the first part of the experiments, that is, so long as the pressure in the boiler was smaller than, say, half of the external pressure; but as soon as the pressure was greater a low rushing could be heard; the passage of the experiment from the first part into the second part (see preceding tabulation) could be determined by the ear. The efflux of air under high pressure into the free atmosphere takes place, as is well known, with a powerful, roaring, noise.

#### § 48. EXPERIMENTS ON THE FLOW OF AIR THROUGH LONG CYLINDRICAL PIPES; MOTION AGAINST GREAT RESISTANCES.

The investigation of the motion of gases in pipes is of technical importance. In most cases we have to do with such slight differences of pressure that we can regard the specific volume of the gas at all places of the pipe line as approximately invariable. Experience has shown that it is thoroughly reliable to determine the velocity of the flowing quantity of gas or air exactly according to the formulas found for the motion of water in pipes, and to use then the same coefficient of resistance in the calculation.

But hitherto there have been no experiments whatever which would enable one to draw a conclusion as to the behavior of air

when flowing through a long pipe toward a vacuum or to a highly rarefied space. Of interest here is the question as to the velocity and the condition of the air in the efflux opening, and of interest also is the law of the resistances which must be used in the calculation. It is at once evident that a rapid diminution of pressure and a marked expansion of the air, with rapid increase of velocity, will here take place on the way to the orifice, but it is also evident that the hypothesis employed with simple orifices, namely, that the air expands polytropically, is no longer permissible.

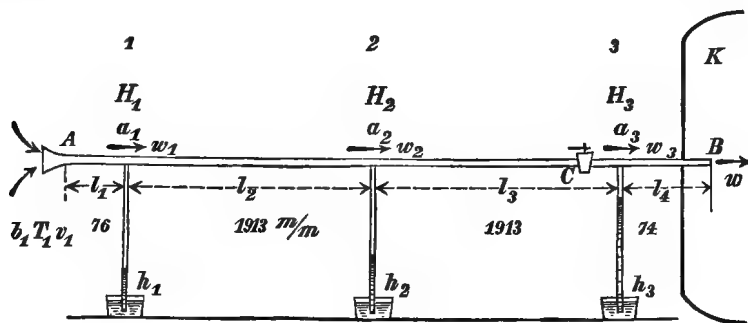


FIG. 40.

Now I have modified the experimental arrangement above described in such a way that atmospheric air could flow through pipes of different length into the air-boiler. In the following will now be described the results of a series of experiments in which the air went through a smooth pipe of  $d=5.1$  mm. diameter [0.201 in.] and of a length of about 4 m. [13.045 ft.].

The outer end A of the pipe (Fig. 40) was provided with a well-rounded influx orifice through which the outer air entered into the pipe. The other end B of the pipe projected for a short distance into the interior of the air-boiler K. At the beginning of the experiment the cock C was completely opened, and it was closed at the end.

At the places designated by 1, 2, and 3 there were vacuum gauges, glass tubes which at their upper ends opened into the interior of the pipe, and at their lower ends dipped into mercury. During the flow of the air the level of the mercury columns occupied the heights  $h_1$ ,  $h_2$ , and  $h_3$ , and at a given signal these were simul-

taneously read by three observers; these heights, subtracted from the barometer reading, gave the piezometer readings, the pressure of the air at the three places in millimeters of mercury, and in the following are designated by  $a_1$ ,  $a_2$ , and  $a_3$ .

The first part of the results of the observations is given in the following table, which after the above description needs no further explanation.

### Straight Line of Pipe.

Diameter 5.1 mm. [0.2008 in.], cross-section  $F=20.428 \times 10^{-6}$  qm. [0.03166 sq. in.], total height  $l=3.976$  m. [13.045 ft.], barometer reading  $b_1=750.3$  mm. [29.54 in.], temperature of air,  $T_1=273+23.2=296.2^\circ$  [533.16°], dew point  $T_0=273+17=290^\circ$  [522°], and corresponding steam pressure is  $b_0=14.42$  mm. [0.5677 in.].

Number of Experiment	Duration of Flow $t'$	Equilibrium Pressure $b_2$ $b_3$	Value of $\frac{b_3-b_2}{t}=\phi$
1	182.5	22.6 mm.	0.2110
2	187.0	61.1	0.2139
3	183.3	101.1	0.2128
4	181.8	140.1	0.2118
5	182.0	178.1	0.2099
6	184.5	216.8 255.0	0.2070

We see that in the first experiments the value of  $\phi$  is approximately constant, but shows a tendency to decline from the fifth experiment on; the experiments were, to be sure, carried farther, but for the following purposes the given data will suffice.

From the data just given for the short orifice we can compute the vapor pressure and find it to be  $b''=14.73$ , the constant  $B_m=29.482$  [53.639], also the specific weight  $\gamma_1$  and the specific volume  $v_1$  of the external atmospheric air, namely,

$$\begin{aligned} \gamma_1 &= 1.1681 \text{ kg.} & \text{and} & & v_1 &= 0.8561 \text{ cbm.} \\ [\gamma_1 &= 0.07292 \text{ lb.} & \text{and} & & v_1 &= 13.714 \text{ cu. ft.}] \end{aligned}$$



The cubic capacity  $V$  of the vessel is  $V=4.2290$  cbm.<sup>1</sup> [149.35 sq. ft.], the mean value of  $\phi$  of the first four experiments is  $\phi=0.2124$ , and we therefore get with the given values, from equation (55),

$$\frac{G}{F}=68.456 \text{ kg. [14.021 lb.]}$$

for the weight of air per sq. meter [sq. ft.] which passes in one second through the efflux orifice. In the well-rounded orifice of the same cross-section this was found according to p. 269 to be 229.1 kg. [46,923 lb.]; we see from this how greatly the pipe resistances reduce the quantities flowing through.

For the same series of experiments there were simultaneously read in each individual experiment the three vacuum gauges during the flow of the air; the first reading was taken 30 seconds after the opening of the cock, and also after 60, 120, and 150 seconds. The following tabulation gives the corresponding piezometer readings only for the time corresponding to 30 and 150 seconds, and was determined from the readings of the vacuum gauge.

Number of Experiment	Time after Opening the Cock.	Piezometer Reading.		
		$a_1$	$a_2$	$a_3$
1	30''	725.8	545.3	192.7
	150	725.8	545.3	192.7
2	30	725.8	545.3	192.7
	150	725.8	545.3	192.7
3	30	725.9	545.8	194.3
	150	725.9	546.2	198.3
4	30	726.0	546.6	202.8
	150	726.0	548.3	215.8
5	30	726.3	549.4	224.3
	150	726.7	552.4	242.8
6	30	726.9	554.4	251.8
	150	727.4	558.9	273.1

<sup>1</sup> During respective calibrations of the vessels of different temperatures there was found for the vessel capacity  $V=4222.04+0.3\tau$  cbdm for water at the temperature of  $\tau^\circ\text{C}$ .

We see that the pressures in the pipe maintain themselves at the same heights during the first two experiments; a marked rise of piezometer reading No. 3 only occurs with the third and fourth experiments. From experiment 5 the values  $a_1$ ,  $a_2$ , and  $a_3$  grow with the increasing boiler pressure.

If at any place of the pipe  $p$  is the pressure,  $v$  the specific volume, and  $w$  the velocity of the air, we shall have, according to equation (7), p. 234, the relation

$$H = \frac{w^2}{2g} = \frac{\kappa}{\kappa-1}(p_1 v_1 - pv), \dots \dots \dots (56)$$

where  $H$  represents the energy of flow. But now the relation  $Gv = Fw$  holds, and as the same quantity  $G$  flows through all cross-sections, and because in a cylindrical pipe all cross-sections  $F$  are of the same size, we get also for the ratio  $G:F$  a constant which we will designate by  $\lambda$ , and there follows

$$\lambda = \frac{G}{F} = \frac{w}{v}, \dots \dots \dots (57)$$

which value for the first four experiments in our case leaves  $\lambda = 68.456$  [14.021]. The combination of the two preceding equations gives

$$\frac{\lambda^2 v^2}{2g} = \frac{\kappa}{\kappa-1}(p_1 v_1 - pv). \dots \dots \dots (58)$$

Now since  $p_1 v_1$  is known for the exterior air and  $p$  is determined by the piezometer reading  $a$  by means of the equation  $p = 13.596a$  [ $p = 70.73a$ ], we can compute, from equation (58), for the bodies in question the specific volume  $v$ , then, according to equation (57),  $w = \lambda v$ , and next get  $H = w^2 : 2g$ , or the energy of flow at this place.

In this way there was found (Fig. 40) for the three piezometers respectively

$a_1 = 725.8,$	$a_2 = 545.3,$	$a_3 = 192.7 \text{ mm.}$
$v' = 0.8809,$	$v'' = 1.1635,$	$v''' = 3.0819 \text{ cbm.}$
$w_1 = 60.30,$	$w_2 = 79.65,$	$w_3 = 210.98 \text{ m.}$
$H_1 = 185.3,$	$H_2 = 323.4,$	$H_3 = 2268.7 \text{ mkg.}$

From this can be seen that particularly in the portion from 2 to 3 there is great expansion of the air and great increase of velocity.

Now it is a question of taking into account the resistances to motion in the pipe.

If in equation (58) we temporarily make  $\frac{(\kappa-1)\lambda^2}{2g} = c$ , then we shall have

$$cv^2 = p_1 v_1 - pv,$$

and from this

$$p dv = p_1 v_1 \frac{dv}{v} - c v dv,$$

or also, because the differentiation of equation (59) gives

$$2cv dv = -d(pv),$$

we get

$$p dv = \frac{1}{2} d(pv) + p_1 v_1 \frac{dv}{v}. \quad . \quad . \quad . \quad . \quad . \quad (60)$$

But the work of resistance  $dW$  must be written, according to equation (IIc), p. 234, as follows:

$$dW = \frac{d(pv)}{\kappa-1} + p dv,$$

and with equation (60) we get

$$dW = \frac{(\kappa+1)}{2(\kappa-1)} d(pv) + p_1 v_1 \frac{dv}{v},$$

or, if we utilize equations (56) and (57),

$$dW = \frac{p_1 v_1}{2} \frac{dH}{H} - \frac{\kappa+1}{2\kappa} dH.$$

If in addition we introduce  $H_0$  as an auxiliary quantity with the significance

$$H_0 = \frac{\kappa}{\kappa+1} p_1 v_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

there finally follows

$$dW = \frac{\kappa+1}{2\kappa} \left( H_0 \frac{dH}{H} - \bar{a}H \right) . \quad . \quad . \quad . \quad (62)$$

The equation can be integrated. In our case the work of resistance  $W'$  on the way from the first to the second piezometer (Fig. 40) is found to be

$$W' = \frac{\kappa+1}{2\kappa} \left( H_0 \log_e \frac{H_2}{H_1} - (H_2 - H_1) \right),$$

and the work  $W''$  on the way from the second to the third piezometer

$$W'' = \frac{\kappa+1}{2\kappa} \left( H_0 \log_e \frac{H_3}{H_2} - (H_3 - H_2) \right).$$

The auxiliary quantity  $H_0$  is found from equation (61) to be

$$\begin{aligned} H_0 &= 5109.2 \\ [H_0 &= 16,763 \text{ ft-lb.}] \end{aligned}$$

and according to the tabulation on p. 275 there follows

$$\begin{aligned} W' &= 2312 \text{ mkg.}, & W'' &= 6844 \text{ mkg.} \\ [W' &= 7585.4 \text{ ft-lb.} & W'' &= 22454 \text{ ft-lb.}] \end{aligned}$$

referred to the unit of weight of air.

The piezometers are equally far apart, and in our case (Fig. 40)  $l_2 = l_3 = 1.913$  m. [6.2763 ft.]; therefore, in the second half of the way, the work of resistance is almost three times as great as in the first half.

For the further investigation of the problem it is now necessary, in judging of the resistances, to start from a particular hypothesis.

For the motion of water, in a cylindrical pipe of diameter  $d_r$  and length  $l$ , we can calculate the loss of energy, in consequence of friction, by the formula

$$\zeta_r \frac{l}{d_r} \frac{w^2}{2g} = \zeta_r \frac{l}{d_r} H,$$

where the velocity  $w$  of the water and the energy of flow  $H$  are the same in all cross-sections, and where  $\zeta_r$  represents the coefficient of resistance, the so-called coefficient of friction of the pipe, which on the average is constant, is commonly taken  $\zeta_r=0.025$ . With air, to be sure, under the assumption of small differences of pressure, the same hypothesis is generally employed; now in what follows it will be assumed that in the present case also  $\zeta_r$  can be regarded, on the average, as a constant quantity. As  $H$  varies greatly, the foregoing formula is only valid for an elementary length  $dx$ , consequently we must put

$$dW = \zeta_r \frac{H}{d_r} dx;$$

introducing the auxiliary quantity  $\alpha$  with the meaning

$$\frac{2\kappa}{\kappa+1} \frac{\zeta_r}{d_r} = \alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

we get, from the preceding equation and with the help of equation (62),

$$\begin{aligned} \alpha dx &= H_0 \frac{dH}{H^2} - \frac{dH}{H}, \\ \alpha dx &= -d \left[ \frac{H_0}{H} - \log_e \frac{H_0}{H} \right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (64) \end{aligned}$$

If we designate the quantity in the bracket by  $X$ , and in the present case introduce for the three piezometer readings the above values of  $H_1$ ,  $H_2$ , and  $H_3$ , there will follow

$$X_1 = 24.249, \quad X_2 = 13.040, \quad X_3 = 1.440.$$

Integration of equation (64) will respectively give for the passage from the first to the second piezometer, and for the passage from the first to the third piezometer (Fig. 40),

$$\alpha l_2 = X_1 - X_2 = 11.209 \quad \text{and} \quad \alpha(l_2 + l_3) = X_1 - X_3 = 22.809.$$

Measurement gives  $l_2 = l_3 = 1.913$  m. [6.2763 ft.], hence we have, respectively,  $\alpha = 5.862$  [1.7867] and 5.965 [1.818], and because

$d_r=0.0051$  m. [0.01673 ft.], equation (63) will give the coefficient of resistance  $\zeta_r$  for the two pipe intervals, namely,  $\zeta_r=0.0256$  and  $\zeta_r=0.0260$  respectively, which are very nearly the same; the reliability of the hypothesis employed is therefore established and  $\zeta_r$  is shown to be a nearly constant value, as with water.

If we again start from the first piezometer, but go on to the orifice of efflux for which  $H$  represents the energy of flow, we get

$$\alpha(l_2+l_3+l_4)=X_1-X,$$

and because  $l_4=0.074$  [0.2428 ft.] (Fig. 40), we have

$$X=\frac{H_0}{H}-\log_e \frac{H_0}{H}=24.249-3.900\alpha$$

$$[X=24.249-12.795\alpha],$$

substituting here  $\alpha=5.965$  [ $\alpha=1.818$ ], there results  $X=0.986$ , a value differing but little from unity. The smallest changes of the separate quantities, lying wholly within the errors of observation, lead to the value  $X=1$ , which in principle is the minimum value.

With the help of equation (61) it therefore follows that

$$H=H_0=\frac{\kappa}{\kappa+1}p_1v_1.$$

The introduced auxiliary  $H_0$  means nothing but the energy of flow in the orifice.

With the help of equation (56) then follows

$$pv=\frac{2}{\kappa+1}p_1v_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

and the efflux velocity

$$w=\sqrt{\kappa g p v};$$

consequently it is equal to the acoustic velocity corresponding to the state of the air in the plane of the orifice.

With it is also found

$$w = \sqrt{\frac{2g}{\kappa+1} B_m T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

For the present case, calculation gives  $w=316.6$  m. [1038.7 ft.]; furthermore from equation (57) the volume  $v$  in the orifice becomes  $v=\frac{w}{\lambda}=4.6250$  [74.088 cu. ft.], and equation (65) gives the pressure there as  $p=1567$  kg. [320.94 lb.] or  $b=115.2$  mm. [4.535 in.], and for the pressure ratio

$$\frac{p}{p_1} = 0.1536,^1$$

which is a very different value from that given by the well-rounded orifice.

Moreover the foregoing equations give directly the orifice pressure

$$p = \lambda \sqrt{\frac{2B_m T_1}{g\kappa(\kappa+1)}},$$

in which of course the value  $\lambda=G:F$  must be given by experiment or must be specially calculated. If  $p_2$  is the pressure in the boiler, then the given propositions hold so long as  $p > p_2$ .

In this case  $X=1$  always, and if the distance of any cross-section of the pipe measured backward from the orifice is designated by  $l$ , and the energy of flow in this cross-section by  $H_x$ , we get, with the help of equation (63),

$$\frac{H_0}{H_x} - \log_e \frac{H_0}{H_x} = 1 + \zeta_r \frac{2\kappa}{\kappa+1} \frac{l}{d_r}, \quad . \quad . \quad . \quad . \quad . \quad (67)$$

<sup>1</sup> Remark. The value given for  $p:p_1$  is valid for a length of pipe of about 4 meters [13.12 ft.], with a diameter  $d_r=5.1$  mm. [0.201 in.]. In another series of experiments, with a pipe half the length and the same diameter there is found  $\frac{p}{p_1}=0.2090$ , and for the well-rounded orifice of the same diameter  $\frac{p}{p_1}=0.5047$  (see p. 251). Therefore if the air is to flow from a boiler into the free atmosphere, then in the three cases the boiler pressure must, respectively, be at least

$$p_1 = 6.51, 4.78, \text{ or } 1.98 \text{ atmospheres}$$

if the air is to flow out with the velocity of sound, as when passing into a vacuum.

from which  $H_x$  can be found (by trial) and then the velocity  $w_x$  determined, in the cross-section under consideration. With the value  $\lambda$  we can also find from  $\lambda v_x = w_x$  the specific volume  $v_x$ , and, with the help of equation (56), there can be found at this place the specific pressure  $p_x$ , so that a picture can easily be made of the variations of  $p_x$ ,  $v_x$ , and  $w_x$  from section to section.

The proposition developed in the foregoing has also been confirmed by experiments on a shorter pipe, so that we may now enunciate the following:

1. If air flows through a long pipe into a vacuum or into a highly rarefied space, the efflux velocity is identical with the acoustic velocity in the orifice, and can be computed according to equation (66) provided pressure, temperature, and moisture of the air in the discharging vessel are known. The efflux velocity is then a maximum and independent of the resistances of the pipe, the latter influencing only the quantity discharged, which becomes smaller as the resistances increase.

2. The resistances in a cylindrical pipe are to be estimated in the same way as with the motion of water, and the corresponding coefficient of resistance or of friction  $\zeta_r$  is also approximately the same; the latter may, as with water, slightly change with the velocity of flow,<sup>1</sup> which, however, should be settled by further experiments with air.<sup>2</sup>

3. For the flow of air through pipes into rarefied spaces, or for the efflux of air with very great excess of pressure, there is still to be established the law according to which the air expands in the pipe; for this purpose the experiments discussed above will not, in general, suffice, and ought to be continued under varied conditions. On the other hand

4. It is thoroughly justifiable to draw from the above adduced experiments the conclusion that the hitherto customary method of treating, for very small differences of pressure, the flowing

<sup>1</sup> Zeuner, "Vorlesungen über Theorie der Turbinen," Leipsic, 1899, p. 50.

<sup>2</sup> Compare Weisbach, "Versuche über Ausströmung der Luft unter hohem Druck," etc., Civilingenieur, Vol. 12, 1866, p. 85.



motion of air in pipes like the motion in water, is a sound method, provided we can regard the specific volume of the air, during the flow, as approximately invariable.

### C o n c l u s i o n .

Recently the theory of the motion of gases has often been the subject of special investigations, but as they principally relate to the flow of s t e a m the whole question will be more fully discussed in the second volume of this treatise; in this connection special reference may be made to the beautiful experimental investigations of S t o d o l a.

# APPLICATIONS.

## TECHNICAL PART.

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### I. On the Theory of Air Engines.

#### § 49. PRELIMINARY REMARKS.

We distinguish between hot-air engines and cold-air engines; the purpose of the former is to transform, on a more or less large scale, heat into work, reliably and continuously, and to utilize this work for technical purposes, for the running of machines engaged in the performance of work.

Hot-air engines are therefore prime movers; they are driven by a gas, the atmospheric air, which is the "motive power" in the mechanical, technical, sense, and the "medium or mediating body" in the thermodynamic sense; the quantity of air enclosed in the engine receives and rejects heat, and in consequence experiences periodically such changes of pressure and volume during expansion and compression that the corresponding pressure curve, or the several pressure curves occurring in the process, constitute an indicator diagram, and enclose an area whose amount gives directly a measure of the work performed during a full period; in a word, the engine describes a cycle. In the cycle of a hot-air engine the performance of work is accompanied by the consumption of heat, as was fully explained in the first section.

During expansion the air withdraws heat from a body of higher temperature, and during compression transfers it to a body of

lower temperature; the difference of the heat received and the heat given off is thereby consumed in doing outer work.

A cycle of the given kind can also be conceived as conducted in the reverse direction, and this case exists in the cold-air engine; here the air during expansion withdraws heat from a body of lower temperature and transfers it during compression to a body of higher temperature; in so doing the quantity of heat given off is greater than the quantity received, and the difference must be generated by work. The running of the cold-air engine requires mechanical work, and the machine therefore belongs to the class of operating machines (Arbeitsmaschinen); its purpose is to withdraw heat, at low temperatures, from certain bodies, to produce cold; at times to cause liquids (water) to freeze and thus form ice. (Ice machines.)

In the one case, in which it is a question of generating work, as in the other case, in which it is a question of producing cold, it does not matter what the medium or mediating body is; if, therefore, in the engines discussed the air is replaced by a mixture of vapor and liquid, we have, in place of an air-engine, the steam-engine, and here we must in like manner distinguish the hot-vapor engine from the cold-vapor engine, according as the cycle is conducted in the one direction or the other.

In all the engines mentioned, which are best designated by the general name "heat engines," we must, according to the construction, distinguish between the two different kinds, the closed and the open engines.

In the closed heat engine the mediating body, air or gas, or a mixture of vapor and liquid of any sort, is confined in the engine, and at the end of the process is brought back to the initial condition in order that it may continually repeat the same process; in the open engine, on the other hand, the mediating body is discharged at the end of each process, i.e., expelled from the engine, and in its place there is taken in, from without, a new quantity of the same medium.

Of course, in the latter case only such mediating bodies are employed as can be found everywhere, without running expenditure; consequently open-air engines are fed with atmospheric air

in the condition (pressure and temperature) of the external atmosphere, while the steam engines are fed with water.

In the engines here discussed, during the cycle described within the engine, no chemical changes take place; the open-air engines dismiss the atmospheric air with another temperature, in general a higher one, and, under certain conditions, with another pressure than it possessed when it was taken in; and in the open steam engine there exists only a change in the state of aggregation, the water that was taken in leaving the engine in the form of steam, or, to speak more correctly, as a mixture of vapor and liquid.

But to the class of heat engines there also belong those engines which are fed by a mixture of bodies, ordinarily gases of various kinds which complete within the working cycle of the engine, and indeed in the interior of the engine itself, a chemical process—combustion, explosion. They will be subjected to investigation later on under the name of internal-combustion engines.

## A. HOT-AIR ENGINES.

### (a) Closed Hot-air Engines.

#### § 50. THE CARNOT CYCLE OF A CLOSED AIR ENGINE.

Let the piston  $K$  and its cylinder  $A$  (Fig. 41) enclose, at the left end of the latter, a space containing  $G$  kg. [lb.] of air; let the volume of the air be  $V_1$ , its pressure  $p_1$ , and  $T_1$  the corresponding absolute temperature; if  $v_1$  is the specific volume we have the relation  $V_1 = Gv_1$ .

If we lay off on the axis  $OX$  the distance  $V_1$  as abscissa, and  $p_1$  as ordinate, then the point  $a$  corresponds to the accompanying temperature  $T_1$  and determines completely the state of the air at the instant.

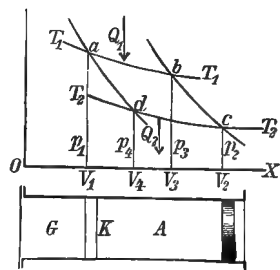


FIG. 41.

With this quantity of air the following cycle will be described, and in so doing we will for the present disregard the question whether it can be practically conducted in this manner.

Let

1. the air expand isothermally, doing work by overcoming an external pressure which constantly corresponds to the pressure of the air at each successive instant (i.e., let it take place in a reversible fashion); in so doing the temperature  $T_1$  of the air remains constant, which presupposes a particular kind of heat supply.

The quantity of heat  $Q_1$ , which must be imparted from the outside to the air during its expansion from  $V_1$  to  $V_3$ , and which is absorbed by the air at the constant temperature  $T_1$ , can be found according to the proposition given in § 26, pp. 137 and 138, from

$$Q_1 = GABT_1 \log_e \frac{p_1}{p_3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

and the quantity of work  $L_1$  thus produced by the expansion of the air is found from

$$L_1 = GBT_1 \log_e \frac{p_1}{p_3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

where  $p_3$  is the pressure corresponding to the point  $b$  and the volume  $V_3$ .

Now lay through the two points  $a$  and  $b$  (Fig. 41) the adiabatic curves  $bc$  and  $ad$  and let

2. the air expand still further without receiving or rejecting heat, till it reaches the point  $c$ , corresponding to the volume  $V_2$ , pressure  $p_2$ , and temperature  $T_2$ . The work  $L_1'$  thus produced is, according to equation (62a), p. 140,

$$L_1' = G \frac{c_v}{A} (T_1 - T_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now let

3. the air be compressed along the isothermal curve  $cd$  at the constant temperature  $T_3$  till it reaches the point  $d$  which has  $V_4$ ,  $p_4$ , and  $T_2$  as volume, pressure, and temperature, and which lies

on the adiabatic passing through  $a$ . In so doing a quantity of heat  $Q_2$  must be withdrawn from the air and a quantity of work  $L_2$  must be expended, which quantities can be found from the following formulas:

$$Q_2 = GABT_2 \log_e \frac{p_4}{p_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

$$L_2 = GBT_2 \log_e \frac{p_4}{p_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

Finally let

4. the air be brought back adiabatically along the path  $da$  to the initial state  $a$ ; the work  $L_2'$  which is necessary for this part of the compression can be found from

$$L_2' = G \frac{C_v}{A} (T_1 - T_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

During this cycle a quantity of heat  $Q_1 - Q_2$  has disappeared and been transformed into work; the net work produced can be found from

$$L = L_1 + L_1' - L_2 - L_2',$$

and by substituting in this the foregoing values we get

$$L = GB \left( T_1 \log_e \frac{p_1}{p_3} - T_2 \log_e \frac{p_4}{p_2} \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the quantities of work  $L_1'$  and  $L_2'$  cancelling each other because of their equality.

The two expressions given for the heat quantities  $Q_1$  and  $Q_2$  of course lead to the relation

$$AL = Q_1 - Q_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

Now, according to the propositions which were found for the adiabatic curve (§ 27, equation 61, p. 139), we have for the two passages  $bc$  and  $ad$ , between the same temperature limits  $T_1$  and  $T_2$ , the relations

$$\frac{T_1}{T_2} = \left( \frac{p_1}{p_4} \right)^{\frac{\kappa-1}{\kappa}} \quad \text{and} \quad \frac{T_1}{T_2} = \left( \frac{p_3}{p_2} \right)^{\frac{\kappa-1}{\kappa}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and therefore between the four pressures there obtains the relation

$$p_1 p_2 = p_3 p_4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in accordance with which, equation (5) gives

$$L = GB(T_1 - T_2) \log_e \frac{p_1}{p_3},$$

and if, besides, we determine  $p_3$  from the second one of equations (6), we get

$$L = BG(T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{\kappa}{\kappa-1}}, \quad . \quad . \quad . \quad . \quad (8)$$

while with the help of relation (7) and equations (1a) and (3a) we find the ratio of the two heat quantities  $Q_2$  and  $Q_1$  to be

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and from this, with the help of equation (5a), we get.

$$L = \frac{Q_1}{AT_1} (T_1 - T_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where

$$\frac{Q_1}{AT_1} = \frac{Q_2}{AT_2} = P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

stands for the change of entropy for the two isothermal passages on the curves  $ab$  and  $dc$  that have taken place between the two adiabatic curves  $bc$  and  $ad$ . The last two equations were already given in the first section, in the general discussion of the *C a r n o t* cycle, and were there designated as (IV) and (V), p. 52, only there the function  $S$  was used in place of the absolute temperature  $T$ , and the identity of the two functions did not appear until the investigations in § 23, p. 130, were made.

Moreover for the case before us the volume of the air can be found for each one of the four vertices of the curved quadrilateral

*abcd* (i.e., for the indicator diagram, corresponding to the C a r n o t cycle) from the formulas

$$\left. \begin{array}{l} V_1 p_1 = G B T_1; \quad V_2 p_2 = G B T_2; \\ V_3 p_3 = G B T_1; \quad V_4 p_4 = G B T_2. \end{array} \right\} \cdot \cdot \cdot \cdot \quad (12)$$

Multiplying the two upper expressions and the two lower ones gives, with the consideration of equation (7), the additional relation

$$V_1 V_2 = V_3 V_4. \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (13)$$

Finally from the second of equations (12) the value  $GB$  can be determined, and utilized in equation (8); we then get the work, which is designated in technical circles as the indicated work per period:

$$L = V_2 p_2 \frac{T_1 - T_2}{T_2} \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{\kappa}{\kappa-1}}. \quad \cdot \cdot \cdot \cdot \quad (14)$$

As  $V_2$  represents the greatest volume, assumed by the air weight  $G$  within the cycle, the preceding equation enables us to draw a conclusion as to the size of the power cylinder necessary for a determinate amount of work  $L$ ; moreover  $p_1$  is the greatest pressure and  $p_2$  the least pressure occurring in the cycle possessing the limiting temperatures  $T_1$  and  $T_2$ .

Now if a hot-air engine is to really describe a cycle like that of Fig. 41, and if not only to the left of the piston  $K$ , but also to the right of it, a quantity of  $G$  kg. [lb.] of air describes the given cycle, so that we have before us a d o u b l e - a c t i n g engine, then there will be described, during every revolution, t w o cycles, during a complete double-stroke of the piston, when the oscillating motion is effected by a crank mechanism. Now if the engine makes  $u$  revolutions per minute, the work performed per second is

$$\frac{2 Lu}{60},$$

and if we divide this value by 75 mkg. [550 ft-lb.] we get the



work produced in horse powers, which will be designated by  $N$ , and then

$$N = \frac{Lu}{30 \times 75} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\left[ N = \frac{Lu}{30 \times 550} \right].$$

If we here utilize equation (14) and let  $F$  represent the piston cross-section (Fig. 41) and let  $s$  represent the total piston stroke, then, disregarding the clearance space, we shall have  $V_2 = Fs$  and accordingly

$$N = \frac{Fsu}{30} \times \frac{p_2}{75} \times \frac{(T_1 - T_2)}{T_2} \log_e \frac{p_1 \left( \frac{T_2}{T_1} \right)^{\frac{\kappa}{\kappa-1}}}{p_2} \quad . \quad . \quad (16)$$

$$\left[ N = \frac{Fsu}{30} \times \frac{p_2}{550} \times \frac{(T_1 - T_2)}{T_2} \log_e \frac{p_1 \left( \frac{T_2}{T_1} \right)^{\frac{\kappa}{\kappa-1}}}{p_2} \right].$$

This is the equation of work for this double-acting engine in the form in which it would be directly used in technical investigations, provided the cycle treated here could be practically realized in the manner described.

But of equal technical importance is equation (10), which gives the relation between the produced work  $L$  and the heat quantity  $Q_1$ , which is absorbed during isothermal expansion  $ab$  of the air confined in the engine. If in equation (10) we reduce the heat quantity to the second, and designate it by  $Q_1''$ , then  $L$  will represent the work produced in one second, expressed in meter kilograms [ft.-lbs.], and if we designate this work expressed in horse-powers by  $N$  we shall get

$$N = \frac{Q_1''}{75 \times AT_1} (T_1 - T_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$\left[ N = \frac{Q_1''}{550 AT_1} (T_1 - T_2) \right].$$

From equation (9) there will then follow the heat quantity  $Q_2''$ , which on the average must be given off to the outside, during every second, by the working air during its isothermal compression along the path  $cd$  (Fig. 41), namely,

$$Q_2'' = \frac{T_2}{T_1} Q_1'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Closely connected with the foregoing investigations is the question whether, and under what circumstances, it is possible to apply the *C a r n o t* cycle to actually constructed engines.

If first of all we consider only air-engines, we recognize at once that it is impossible to carry through, in one and the same cylinder, the four separate parts of the cycle described in Fig. 41.

Now as regards the first two parts of the cycle; during the first part, along the path *ab*, the air is to be heated at the constant upper temperature  $T_1$ , and during the second part along the path *bc* it is to expand *a d i a b a t i c a l l y*, till the lower temperature limit  $T_2$  is reached; even this requirement cannot be fulfilled because of the influence of the cylinder walls, for in the second part of the cycle these would take part in the adiabatic lowering of temperature, by imparting heat to the air; still less can the third and fourth parts of the cycle be carried on in the same space.

These difficulties can, however, be overcome, at least in part, and are in fact approximately circumvented in the practical designs of the air-engine (as in the steam-engine) by having the separate parts of the cycle take place, in at least two spaces, but mostly in three different spaces, by shifting the working quantity of air from one space to the other and by designing, for this purpose, engine arrangements which will be discussed later.

Still another point is worthy of note. Equation (8) gives the work produced by the engine, but this formula has a positive value only when the value under the logarithmic sign is greater than unity, therefore the condition

$$\frac{p_1}{p_2} > \left( \frac{T_1}{T_2} \right)^{\frac{\kappa}{\kappa-1}}$$

must be satisfied; but  $p_1$  represents the greatest, and  $p_2$  the least, pressure occurring in the cycle (Fig. 41), consequently these limiting pressures must fulfill certain conditions, prescribed by the limiting temperatures. For example, if we assume  $t_1=350^\circ$  C. [ $662^\circ$  F.] as the highest permissible temperature, and  $t_2=15^\circ$  C. [ $59^\circ$  F.], so that  $T_1=623^\circ$  [ $1121.4^\circ$ ] and  $T_2=288^\circ$  [ $518.4^\circ$ ], we shall get

$$\frac{p_1}{p_2} > 14.20.$$

The engine must therefore work between very wide pressure limits, which would separate still further if we wished to, and could, extend the temperature limits.

The practical construction of the Carnot cycle in air-engines is therefore not feasible (in steam engines the conditions are far more favorable); nevertheless here, as later investigations will show, the application of the so-called regenerators offers a means of constituting the conditions more favorably.

### § 51. THE CLOSED AIR-ENGINE CYCLE BETWEEN TWO PAIRS OF POLYTROPIC CURVES.

Let  $G$  kg. [lb.] of air be confined in the cylinder  $A$  (Fig. 42) to the left of the piston, and let the initial volume be  $V_4$ , the pressure  $p_4$ , and  $T_2$  the temperature; with this quantity of air the

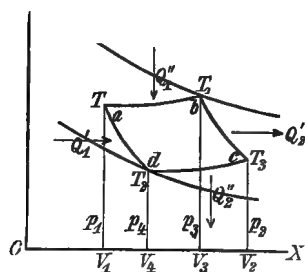


FIG. 42.

cycle  $dabc$  is to be described; here let  $da$  and  $bc$  be two polytropic curves, subject to the law  $pv^{n_1} = \text{constant}$ , and let  $ab$  and  $cd$  be like curves, following the law  $pv^{n_2} = \text{constant}$ . For the first and for the second pair, therefore, the specific heats  $c_1$  and  $c_2$  respectively become (according to equation (4), p. 152)

$$c_1 = \frac{n_1 - \kappa}{n_1 - 1} c_v \quad \text{and} \quad c_2 = \frac{n_2 - \kappa}{n_2 - 1} c_v. \quad (19)$$

Now let  $T_2$ , at the point  $d$ , be the lowest, and  $T_1$ , at the point  $b$ , the highest temperature occurring in the whole cycle, and accordingly the temperatures  $T$  and  $T_3$ , corresponding to the vertices  $a$  and  $c$ , will lie between the limiting values.

From the propositions given in § 29, p. 152, concerning the polytropic curves, we can find the heat quantities  $Q_1'$  and  $Q_2'$ , per unit of weight of air, which must respectively be supplied and withdrawn along the paths  $da$  and  $bc$ , by using equation (6), p. 153,

$$Q_1' = c_1(T - T_2) \quad \text{and} \quad Q_2' = c_1(T_1 - T_3),$$

and similarly for the distances  $ab$  and  $cd$

$$Q_1'' = c_2(T_1 - T) \quad \text{and} \quad Q_2'' = c_2(T_3 - T_2).$$

Consequently the total heat quantity  $Q_1$  which is absorbed by  $G$  kg. [lb.] of air is

$$Q_1 = G[c_1(T - T_2) + c_2(T_1 - T)], \quad . \quad . \quad . \quad (20)$$

and the quantity of heat  $Q_2$  which it rejects is

$$Q_2 = G[c_1(T_1 - T_3) + c_2(T_3 - T_2)]. \quad . \quad . \quad . \quad (21)$$

By utilizing equation (7), p. 153, there can easily be determined the quantities of work which correspond to the separate lengths of the curves; these quantities, properly collected, readily give the work  $L$ , corresponding to the complete cycle:

$$AL = (c_2 - c_1)G[T_1 - T + T_2 - T_3], \quad . \quad . \quad . \quad (22)$$

an equation which also follows from the difference of  $Q_1 - Q_2$  of the two equations (20) and (21).

The four temperature values occurring in these formulas bear a simple relation to each other.

If through the points  $d$  and  $b$  (Fig. 42) we pass adiabatic curves, then for every passage from any point of the first to any point on the second adiabatic the change of entropy

$$P = \int \frac{dQ}{AT}$$

is the same.

For the present case, therefore, along the path  $dab$  (referred to the unit of weight) we get

$$AP = \int_{T_2}^T c_1 \frac{dT}{T} + \int_T^{T_1} c_2 \frac{dT}{T},$$

and for the passage along the path  $dcb$

$$AP = \int_{T_2}^{T_3} \frac{c_2 dT}{T} + \int_{T_3}^{T_1} \frac{c_1 dT}{T}.$$

The integration of these expressions is simple, because in polytropic change  $c_1$  and  $c_2$  are constants and, by equating the two expressions, we can easily get

$$c_1 \log_e \frac{TT_3}{T_1 T_2} = c_2 \log_e \frac{TT_3}{T_1 T_2},$$

and this relation can only obtain, because  $c_1$  and  $c_2$  have different values, when the quantity under the logarithmic sign is equal to unity, consequently only when

$$TT_3 = T_1 T_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

According to equation (5), p. 153, there must exist for the curve portions  $ad$  and  $bc$  the relations

$$\frac{T}{T_2} = \left( \frac{V_4}{V_1} \right)^{n_1-1} \quad \text{and} \quad \frac{T_1}{T_3} = \left( \frac{V_2}{V_3} \right)^{n_1-1};$$

hence, considering the preceding equation (23), we also get

$$V_3 V_4 = V_1 V_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and from this readily the connection

$$p_3 p_4 = p_1 p_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If we suppose the limiting temperatures  $T_1$  and  $T_2$  given, then for any intermediate temperature  $T$  we can get from equation (23) the second intermediate temperature  $T_3$ , and if we substitute these values in equation (22) we get, after a simple reduction, the work  $L$  in the present cycle

$$AL = \frac{G(c_2 - c_1)}{T} (T_1 - T)(T - T_2). \quad . \quad . \quad . \quad . \quad (26)$$

If the exponents  $n_1$  and  $n_2$  are known, for two pairs of polytropic curves, and hence the corresponding specific heats  $c_1$  and  $c_2$  according to equations (19), we can compute from the preceding formula the work  $L$  which is produced by the present cycle, provided the limiting temperatures  $T_1$  and  $T_2$ , and the intermediate temperature  $T$ , are known, and when there is also given the weight  $G$  of the working air; then from equations (20) and (21) there can be found, for each individual operation, the quantity of heat  $Q_1$  which is absorbed, and the quantity  $Q_2$  which is rejected, by the working air. Finally if of the four pressures  $p_1, p_2, p_3, p_4$  a single one is known, for example  $p_1$ , then the others can easily be found; with the help of equation (5), p. 153, there can be found, say,  $p_4$  and  $p_3$  from the relations

$$\frac{p_4}{p_1} = \left(\frac{T_2}{T}\right)^{\frac{n_1}{n_1-1}} \quad \text{and} \quad \frac{p_3}{p_1} = \left(\frac{T_1}{T}\right)^{\frac{n_2}{n_2-1}}. \quad . \quad . \quad . \quad (27)$$

Pressure  $p_2$  then results from equation (25). Finally the volume of the air for each of the four vertices of the indicator diagram (Fig. 42) is determined by the general equation

$$Vp = GBT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

when we substitute in it the corresponding values of  $p$  and  $T$ .

The preceding investigations embrace, according to the choice of the exponents  $n_1$  and  $n_2$ , in the equations of the polytropic curves, or of the corresponding values of the specific heats  $c_1$  and  $c_2$ , an infinite number of separate cases, and give rise to special investigations.

Let us assume for once that one of the pairs of curves, for example  $ad$  and  $bc$ , is made up of adiabatic curves; in this case  $c_1 = 0$ , and there results from equations (26) and (20)

$$AL_1 = \frac{c_2 G}{T} (T_1 - T)(T - T_2),$$

$$Q_1 = c_2 G (T_1 - T),$$

and from these, taking into consideration (23),

$$\frac{AL_1}{Q_1} = 1 - \frac{T_2}{T} = 1 - \frac{T_3}{T_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The ratio of the produced work  $L$  to the supplied heat quantity  $Q_1$  depends therefore only on the given limiting temperatures  $T_1$  and  $T_2$  and the arbitrarily chosen intermediate temperature  $T$  or  $T_3$ ; it is accordingly independent of  $Q_1$  and of the two polytropic curves  $ab$  and  $cd$  (Fig. 42). The ratio  $AL:Q_1$ , which may be designated by  $\phi$ , can be called the thermal efficiency (Güteverhältnis), for it states the fraction of the supplied heat  $Q_1$  which is transformed into work. For prescribed values of the temperatures  $T_1$  and  $T_2$  the value of  $\phi$  depends, as equation (29) shows, on the choice of the intermediate temperature  $T$  and becomes greater, and therefore the cycle so much the more favorable, the larger  $T$  is assumed to be. The greatest permissible value is  $T=T_1$ ; with this value we get  $T_3=T_2$  from equation (23) and

$$\phi = \frac{T_1 - T_2}{T_1};$$

the maximum  $L_m$  of work is then

$$L_m = \frac{Q_1}{AT_1}(T_1 - T_2),$$

the Carnot cycle stands forth and the two curves  $ab$  and  $cd$  are isothermals, as was to be expected.

The foregoing formulas include almost all cases, even those which have hitherto been separately subjected to investigations by others.

## § 52. CLOSED AIR-ENGINE CYCLE BETWEEN TWO ADIABATICS AND TWO UNLIKE POLYTROPIC CURVES.

### (Lorenz Cycle.)

Let Fig. 42 again be taken as a basis of the discussion and let the two curves  $ad$  and  $bc$  of the curved quadrilateral be adiabatic curves; on the other hand let  $ab$  be a polytropic curve for which the specific heat is  $c'$  and let  $c''$  be a similar magnitude for the other polytropic. Accordingly the exponent  $n$  [from equation (19)] will be different for the two polytropic curves  $ab$  and  $cd$ .

Let the highest and lowest temperatures occurring in the cycle again be  $T_1$  and  $T_2$ , and the intermediate temperatures  $T$  and  $T_3$ .

The quantity of heat  $Q_1$  supplied along the path  $ab$  can then be found from

$$Q_1 = c'G(T_1 - T), \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

when  $G$  is the weight of the mediating body, here the air in the working cylinder.

Along the path  $cd$  the heat quantity  $Q_2$  is to be withdrawn and can be determined by the equation

$$Q_2 = c''G(T_3 - T_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

and the work produced is found from

$$AL = G[c'(T_1 - T) - c''(T_3 - T_2)]. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

But the four temperature values are again related to each other in a particular way. For the passage, from the one adiabatic to the other along one or the other polytropic curve, the change of entropy is the same, and therefore we have the relation

$$c' \int_T^{T_1} \frac{dT}{T} = c'' \int_{T_2}^{T_3} \frac{dT}{T},$$

or

$$c' \log_e \frac{T_1}{T} = c'' \log_e \frac{T_3}{T_2}. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

To simplify let us put

$$m = \frac{c'}{c''}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

then follows

$$\frac{T_3}{T_2} = \left( \frac{T_1}{T} \right)^m, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

from which the second intermediate temperature  $T_3$  can be calculated, when a choice has been made of the first one,  $T$ .



Combining equations (30) and (32) then gives the thermal efficiency:

$$\phi = \frac{AL}{Q_1} = 1 - \frac{(T_3 - T_2)}{m(T_1 - T)}, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

or with the use of equation (35)

$$\phi = 1 - \frac{T_2}{mT^m} \frac{(T_1^m - T^m)}{(T_1 - T)}. \quad . \quad . \quad . \quad . \quad . \quad (36a)$$

The equation shows that here also there is a best intermediate temperature  $T$  for which  $\phi$  becomes a maximum. On the other hand if the two polytropic curves are of the same kind then  $m=1$ , and there results, as before, equation (29), which in the most favorable case, for  $T=T_1$ , leads back to the C a r n o t cycle.

The cycle just discussed was first fully treated by L o r e n z.<sup>1</sup>

In all of the preceding investigations there were only considered the changes of state of the m e d i a t i n g body (medium), for example the air enclosed in the engine, but that body was not considered which imparted the heat during the heat supply, and just as little was the body considered which withdrew the heat during the withdrawal of heat. The first body we will call the h e a t i n g body and the other the c o o l i n g body.

Now if we return to the cycle in question (Fig. 42) we find along the path  $ab$  a rise of temperature from  $T$  to  $T_1$ . If we suppose of the heating body in a unit of time, for example in an hour, the weight  $K_1$  to flow past the heating surface, and that its specific heat is  $c_1$ , and that in so doing it c o o l s from  $T_1$  to  $T$ , then the quantity of heat  $Q_1$  which it thus gives off is

$$Q_1 = c_1 K_1 (T_1 - T). \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Similarly if in the same time the cooling body  $K_2$  flows along the cooling surface, and if its specific heat is  $c_2$ , and if in so doing

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<sup>1</sup> H. L o r e n z, "Beiträge zur Beurteilung von Kühlmachines," Zeitschrift des Vereins deutscher Ingenieure, 1894, Vol. 38, pp. 62, 98, and 124.

this body is heated from  $T_2$  to  $T_3$ , thus absorbing the quantity of heat  $Q_2$ , we have

$$Q_2 = c_2 K_2 (T_3 - T_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

From the combination of equations (30) and (31) there consequently follows

$$c'G = c_1 K_1 \quad \text{and} \quad c''G = c_2 K_2, \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where, to be sure, both specific heats  $c_1$  and  $c_2$  must be regarded as constants.

In equations (39)  $G$  signifies the weight of the mediating body referred to the same unit of time, i.e., the hour, which is also assumed for the weights  $K_1$  of the heating body and  $K_2$  of the cooling body. If we consider a double-acting engine, and if  $G$  kg. [lb.] of the mediating body work on each side of the piston, and if the engine makes  $u$  revolutions per minute, then we must substitute  $120 Gu$  in place of  $G$ , in equations (39).

From equations (39) with the help of equation (34) follows

$$m = \frac{c'}{c''} = \frac{c_1 K_1}{c_2 K_2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

if the separate quantities on the right side of this equation are known, and if the temperatures  $T_1$ ,  $T_2$ , and  $T$  are given, then  $m$  can be calculated and also, from equation (35), the second intermediate temperature  $T_3$ , and thus are obtained the propositions of L o r e n z, in which for the present it is not necessary to think of the mediating body.

Moreover, if there is known for the mediating body in the cycle (Fig. 42), even for one vertex of the curved quadrilateral, the corresponding pressure, for example  $p_1$ , then the other pressures can easily be calculated, as soon as  $c'$  and  $c''$  are known and hence as soon as the corresponding exponents  $n'$  and  $n''$  are known from equation (19). With the given temperatures  $T$ ,  $T_1$ , etc., and with  $G$ , there can easily be calculated the volumes  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$ , according to the earlier propositions.

**Example.<sup>1</sup>** In the engine let the heating body consist of fire-gases resulting from the combustion of coal (Steinkohlen) which flows past the heating surface and gives off heat to the mediating body. Let the temperature of combustion upon the grate be  $t_1 = 1227^\circ \text{ C.}$  [ $2240.60^\circ \text{ F.}$ ], and the temperature at the entrance into the uptake be  $t = 227^\circ \text{ C.}$  [ $440.4^\circ \text{ F.}$ ], then  $T_1 = 1500^\circ$  [ $2700^\circ$ ] and  $T = 500^\circ$  [ $900^\circ$ ]; let the specific heat at constant pressure be  $c_1 = 0.24$ , and the weight per hour be  $K_1 = 10500 \text{ kg.}$  [ $23069 \text{ lb.}$ ]. Let the cooling body be water, having the initial temperature  $t_2 = 20^\circ$  [ $68^\circ \text{ F.}$ ], and therefore  $T_2 = 293^\circ$  [ $527.4^\circ$ ], whose hourly weight is  $K_2 = 80000 \text{ kg.}$  [ $176370 \text{ lb.}$ ], and let its specific heat be  $c_2 = 1$ .

Here there is found from equation (40)  $m = 0.0315$ , and then according to equation (35) the final temperature of the cooling water is  $T_3 = 303.2^\circ$  [ $545.76^\circ$ ] or  $t_3 = 30.3^\circ \text{ C.}$  [ $86.54^\circ \text{ F.}$ ], and consequently the rise of temperature  $t_3 - t_2 = 10.3^\circ \text{ C.}$  [ $18.54^\circ \text{ F.}$ ].

From equation (36) can then be calculated the thermal efficiency (coefficient of work)  $\phi = 0.673$ .

**Lorenz** wishes to substitute the here discussed cycle in place of the **Carnot** cycle, and thus raises anew a question which has been so often discussed since the laws of thermodynamics have been employed in judging the heat-engine; he seeks to derive a so-called **perfect cycle**, in which the maximum of work is produced.

### § 53. THE DISPOSABLE WORK OF HEAT ENGINES.

This is the most suitable place to discuss somewhat more thoroughly the question indicated, but we must expressly emphasize in advance that for the present we will consider only those engines in which the heat imparted to, or withdrawn from, the mediating body takes place through walls, as is the case in steam and air engines. The circumstances are different with engines in which the processes of combustion and work take place simultaneously in the interior of the engine, as is the case in gas and internal-combustion engines. The latter engines will not be considered for the present.

In what has preceded it has been repeatedly emphasized, and very specially so, when deriving the fundamental equations of thermodynamics in Section I, p. 53, and in § 50, p. 288, that

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<sup>1</sup> See **Lorenz**, *ibid.* p. 126.

the maximum of work is produced with the Carnot cycle, but in so doing it was expressly provided that the assumed limiting temperatures  $T_1$  and  $T_2$  should refer to the mediating body (medium), consequently, in the air-engine, to the air enclosed in the engine, and so  $Q_1$  is the quantity of heat which the air during its expansion under the constant highest temperature  $T_1$  absorbs, and  $Q_2$  the quantity of heat which it gives off during compression at the constant lowest temperature  $T_2$ . The maximum  $L_m$  of work produced corresponds to a particular prescribed value  $Q_1$  and is found from the formula

$$L_m = \frac{Q_1}{AT_1} (T_1 - T_2), \quad . . . . . (41)$$

and the entropy  $P$  for both passages is

$$P = \frac{Q_1}{AT_1} = \frac{Q_2}{AT_2}, \quad . . . . . (42)$$

and accordingly we can also write

$$L_m = P(T_1 - T_2). \quad . . . . . (42a)$$

For this quantity  $L_m$  we will introduce the term *disposable work* commonly employed in mechanical engineering. Furthermore we will consider an engine describing the Carnot cycle as a theoretically perfect one. Every deviation of the required cycle leads, for the same value  $Q_1$  and for the same limiting temperatures, in the actually described cycle, to a smaller value of the work  $L$ ; the ratio  $L:L_m$ , designated by  $\eta$  and called the *efficiency* (thermodynamic efficiency), will serve as a measure of the excellence of the engine. The difference

$$L' = L_m - L$$

I call the loss of work which corresponds to the imperfection of the cycle, the quantities themselves being referred to the second of time, as is generally the practice with engines.

If we divide both sides of the preceding equation by  $L_m$ , we get

$$\zeta = 1 - \eta,$$

where  $\zeta$  will hereafter designate the loss of efficiency in consequence of the imperfection of the cycle.

The above equation (41) shows that for the same quantity of heat  $Q_1$  the disposable work is greater the further the temperature limits are apart, the greater therefore the fall of temperature  $T_1 - T_2$ , and equation (42a) makes it evident that the work is measured by the product of this fall and the change of entropy.

With respect to the temperatures  $T_1$  and  $T_2$  we are confined in air engines, which are the only ones considered at present, to very definite limits; as regards the lower temperature limit  $T_2$  we are limited in this particular, in engine running, to the temperature which those bodies possess that are used for cooling, to those bodies, therefore, to which the working body imparts its heat during compression; as here cooling water of atmospheric temperature must be exclusively considered, the lower temperature limit must be the mean temperature of the external atmospheric air, say about  $15^\circ \text{C}$ . [ $59^\circ \text{F}$ .], or  $T_2 = 288^\circ$  [ $518.4^\circ$ ]. As regards the upper limit the kind of construction employed in the engine must be considered; at first, and for the present, it is assumed that the piston moves in the cylinder with the ordinary packing; we cannot raise the upper temperature limit above  $350^\circ \text{C}$ . [ $662^\circ \text{F}$ .] as experience has shown, and therefore not over  $T_1 = 623^\circ$  [ $1121.4^\circ$ ], with respect to the maintenance of the lubricating and packing materials; consequently, according to the assumption made, the fall of temperature will be  $T_1 - T_2 = 335^\circ$  [ $603^\circ$ ] and the maximum value of the coefficient of work (thermal efficiency), designated by  $\phi_m$ , will then be, according to equation (41),

$$\phi_m = \frac{AL_m}{Q_1} = \frac{T_1 - T_2}{T_1} = 0.538,$$

or with  $A = 1.424$  [ $A = 1.772.83$ ] the maximum work is

$$\begin{aligned} L_m &= 228 Q_1 \\ [L_m &= 415.58 Q_1]. \end{aligned}$$

Hence in this perfect cycle there corresponds to every unit of heat the work of 228 mkg. [415.58 ft-lb. per B.t.u.].

If we consider a continuously working engine and express the work  $N_m$  in horse-powers, then equation (41) gives the quantity of heat  $Q_1$  which must be absorbed here by the working air at constant highest temperature, namely,

$$Q_1 = \frac{3600 \times 75 \times A T_1}{T_1 - T_2} N_m$$

$$\left[ Q_1 = \frac{3600 \times 550 \times A T_1}{T_1 - T_2} N_m \right],$$

from which follows, for the assumed temperature limits,  $Q_1 = 1184 N_m$  [ $Q_1 = 4764.6 N_m$ ]; consequently for the present case the absorbed quantity of heat will be 1184 calories [4764.6 B.t.u.] per hour per horse power, while the quantity of heat  $Q_2$  which according to equation (42) represents the quantity of heat which is taken up by the cooling body, likewise per hour per horse power, is given by  $Q_2 = 547$  [2202.6], or generally

$$Q_2 = \frac{T_2}{T_1} Q_1.$$

This latter quantity of heat is not, as was assumed in the older views, to be regarded as a loss, whose removal is to be expected by the discovery of another cycle and by another engine arrangement, but this quantity of heat is in principle technically perfectly worthless, for it is heat of the lowest temperature  $T_2$  which cannot be transferred to other bodies. We see from this that the technical value, i.e., the working value, of the heat is not alone to be measured by the number of heat units which are available, but also according to the temperature; the working value of certain quantities of heat is greater the higher the temperature under which the mediating body working in the engine can take up heat. Clear and simple as the whole question in itself is and must appear to the mechanical engineer, particularly if the analogy is regarded which has been referred to at several places above, nevertheless one still meets views, even at the

present day, which spring from a complete misunderstanding of the laws of the mechanical theory of heat and are to be ranked with views which still cling to the possibility of perpetual motion.

The question is most briefly discussed in the following manner.

During the combustion of one kilogram [pound] of coal (Steinkohlen) there is set free on the average 7500 calories [13,500 B.t.u.] of heat; now since 424 mkg. [772.83 ft-lb.] of work corresponds to a unit of heat, it is erroneously concluded that there is available in a unit of weight of such coal a work of  $424 \times 7500 = 3180000$  mkg. [10433230 ft-lb.] of work, and that it is simply the problem of the mechanical engineer to conceive of an engine which will as completely as possible utilize this work. Now in the construction of steam engines (Woolf and Compound-Receiver Engines with jackets) progress has been made which corresponds with the progress made in Watt's time, and of which mechanical engineers may be proud; but these best engines do not even give one-tenth of the work just calculated, and therefore, it is said, there is no reason for viewing with satisfaction the progress mentioned.

If, for comparison, we imagine that at a particular place on a river which flows from the mountains of the interior to the sea there exists an hydraulic plant with head-race and tail-race—the levels of the two races lying respectively  $T_1$  and  $T_2$  m. [ft.] above the level of the sea, and the weight of water supplied per second through the race is  $P$  kg. [lb.],—then the disposable work of the hydraulic motor is

$$L_m = P(T_1 - T_2),$$

and is therefore to be determined in the same way as the disposable work of the heat engine, according to equations (41) and (42a). For the owner of this water power, the two water-marks, referred to the level of the sea as zero, likewise constitute limiting values, for he will try to maintain, by damming, as high a level as possible in the head-race, as high as the law and his contracts with his neighbor above the plant will permit. On the other hand, he will put the level of the tail-race as low as possible, but will, in so doing, be likewise limited, for of course the water must be

able to flow away, and besides he must deliver the water on the tail-race side at a level prescribed by the rights of his next neighbor below.

In the preceding formula the product  $PT_1$  designates the work delivered from above, and the product  $PT_2$  that which must be given off on the tail-race side, the difference of the two only is available for use, is disposable; now it would be absurd, in the present case, to regard the quantity of work  $PT_2$  as a loss and to estimate the excellence of the erected hydraulic motor by the part of the work  $PT_1$  which it really utilizes; but this procedure would be exactly like said mode of estimating heat engines which is still maintained by a few.

If we introduce the value of  $A$  into equation (41), this can also be written in the following form:

$$L_m = 424Q_1 \left(1 - \frac{T_2}{T_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (41a)$$

$$\left[ L_m = 772.83Q_1 \left(1 - \frac{T_2}{T_1}\right) \right],$$

and from it we recognize that the said erroneous estimate of the disposable work only has a meaning when, in the Carnot cycle, we are able to approach the lower temperature limit  $T_2=0$ , or, measured according to Celsius [Fahrenheit],  $t_2 = -273^\circ$  [ $-459.4^\circ$ ]; but in reality, for the reasons already mentioned, the limit lies much higher and will have to be put in air engines  $t_2=15^\circ$  C. [ $59^\circ$  F.] or  $T_2=288^\circ$  [ $518.4^\circ$ ]; on the other hand, for steam engines in which  $t_2$  represents the temperature in the condenser, it will, on the average, have to be put at  $40^\circ$  C. [ $104^\circ$  F.], i.e.,  $T_2=313^\circ$  [ $563.4^\circ$ ]. (In non-condensing steam-engines  $T_2$  must even be taken equal to  $373^\circ$  [ $671.4^\circ$ ], because steam of atmospheric pressure has the temperature  $t_2=100^\circ$  C. [ $212^\circ$  F.].

So far as the lower limit  $T_2$  is concerned we are, in principle, tied for all time to the given limit, and every thought of bettering the engine by changing these conditions is excluded from the beginning.



The conditions are, however, very different with respect to the upper limit of temperature  $T_1$ ; a glance at equation (41a) shows that, with a prescribed value of  $T_2$ , the work  $L_m$  is greater the higher the temperature  $T_1$ .

Here we must pay strict attention to the hypotheses under which the given formula for the disposable work of heat engines according to Carnot's principle is developed; it has already been most expressly emphasized that the temperature limits  $T_1$  and  $T_2$  refer to the mediating body (medium) and therefore, in air engines, refer to the air working in the engine; an illustration was given above of an air engine with the upper temperature limit  $350^\circ \text{C.}$  [ $662^\circ \text{F.}$ ] or  $T_1 = 623^\circ$  [ $1121.4^\circ$ ], and it was then added that the lubricating and packing materials in the working cylinder of the engine would not permit any higher temperature.

It is just so in steam engines in which the upper temperature limit (temperature of the water and steam in the boiler) does not, for reasons which will be discussed later, even reach the value assumed in the foregoing for the air engine, unless indeed the steam is used in a highly superheated condition.

Objections have been repeatedly made to the here discussed method of determining the maximum work and the disposable work, by considering the changes of state of the mediating body as a basis; they point out that the products of combustion of our heating apparatus possess a higher temperature than the just assumed upper temperature limit  $T_1$ , and that therefore, in our fire gases, there is available a considerably larger amount of work than is indicated in the value  $L_m$ , calculated above. This objection, at first glance, seems to be perfectly justified, for it is very natural to directly compare the work produced in the heat engine with the quantity of fuel consumed.

If for this purpose, however, we should consider the Lorenz cycle discussed in § 52, p. 296, we should have to assume that the highest temperature  $T_1$  occurring within the engine would have to be approximately like the temperature of combustion on the grate, and therefore about  $1500^\circ$  [ $2700^\circ$ ], as in the example on p. 300.

Such an assumption in air engines, and particularly in steam-

engines, is not at all permissible; always remembering the hypothesis that with the mediating body the supply and withdrawal of heat takes place through solid walls. \*

If we consider the C a r n o t cycle with the upper temperature limit  $T_1$ , then the fire gases which flow along the heating surface will possess at the start a far higher temperature, and during the heat supply the heat, in a certain sense, falls unutilized from a higher level to a lower one, and to this free fall there will correspond a loss of work which will be greater the more the cycle of the mediating body differs from the C a r n o t cycle. Now if we compute this loss of work the question will arise whether the loss should be charged against the engine proper, i.e., against the hot-air engine, or steam engine, as constructed at the present day.

This question might be answered in the negative, or, rather, with reference to the engine mentioned, might be met by the following remarks.

Let  $L_0$  be the working value of the heat in the heating body, whose value will be determined later, after special preliminary investigations; furthermore let  $L$  be the work of the engine and  $L_m$  its disposable work determined according to C a r n o t, then we may distinguish between two different efficiencies  $\eta$  and  $\eta_0$ , namely,

$$\eta = \frac{L}{L_m} \quad \text{and} \quad \eta_0 = \frac{L_m}{L_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

of which the former refers to the engine, the latter to the heating plant.

There is no objection to directly comparing the work  $L$  of the engine with the working value  $L_0$  of the heating body, and to designating the ratio of these two quantities as the total efficiency; the two preceding expressions give for this ratio

$$\eta' = \eta \eta_0 = \frac{L}{L_0}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

in what follows  $\eta'$  will represent "the efficiency of the whole plant" or "total efficiency."

For the thorough study of a whole plant it is probably more profitable to divide the discussion in the manner indicated by equations (43). In the value  $\eta$  there is mirrored every constructive change of the engine and every change in its cycle, while the magnitude  $\eta_0$  can be regarded as the measure of the excellence of the heating plant and of the method of heating; only by this separate treatment can it be recognized whether the next effective improvement of a plant, i.e., the raising of its total efficiency, should be attempted in the one or in the other direction, in the motor itself or in the heating plant.

What has here been said expressly refers, as has been repeatedly emphasized, to a particular case of heat engines; it includes the steam engines which work with saturated vapors; for this class, therefore, the further discussions will only consider the C a r n o t cycle as the most profitable one described by the m e d i a t i n g b o d y, or, more generally still, will consider only the cycle described by this body.

In the heat engines here discussed the temperatures arising in the cycle of work cannot be brought into harmony with the temperature values existing in the heating body.

The circumstances are very different in refrigerating machines, in the cold-air and the cold-vapor engines which will be discussed more fully later on. The above-mentioned investigations of L o r e n z are related to these, and his cycle is here in fact to be substituted for the C a r n o t cycle.

Finally, another treatment is demanded for those engines in which the process of combustion and of work combined takes place in the interior of the engine, which engines will receive special consideration below as internal-combustion motors.

# § 54. AIR-ENGINE CYCLE BETWEEN TWO ISOTHERMALS AND A PAIR OF LIKE POLYTROPIC CURVES.

(Reitlinger Cycle.)

The cycle of an air engine represented in Fig. 43 consists of two isothermals,  $ab$  and  $cd$ , of which the former corresponds to the upper temperature limit  $T_1$  and the latter to the lower limit  $T_2$ .

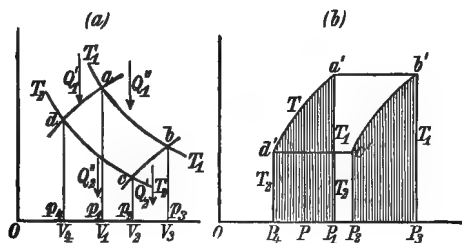


FIG. 43.

The two other curves  $da$  and  $bc$  are two polytropic curves of the same sort obeying the law  $pv^n = \text{constant}$ , whose exponent  $n$  corresponds to the specific heat

$$c = \frac{(n - \kappa)}{(n - 1)} c_v$$

and for the present is to remain undetermined.

This cycle was first investigated by Reitlinger<sup>1</sup> in order to show with its aid under what circumstances the application of a "Regenerator" is possible; this will be discussed later.

If we use the notation given in Fig. 43a, the whole quantity of heat absorbed along the path  $dab$  is

$$Q_1 = Q_1' + Q_1'' = G \left[ c(T_1 - T_2) + ABT_1 \log_e \frac{p_1}{p_3} \right], \quad (45)$$

<sup>1</sup> Reitlinger, "Über Kreisprozesse mit zwei isothermischen Kurven," Zeitschrift des österreichischen Ingenieur- und Architekten-Vereins, 1873.

provided we consider the propositions about the isothermal curves given on p. 137. In like manner we obtain for the quantity of heat  $Q_2$ , given off on the path  $bcd$ , the expression

$$Q_2 = Q_2' + Q_2'' = G \left[ c(T_1 - T_2) + ABT_2 \log_e \frac{p_4}{p_2} \right]. \quad (46)$$

But for the polytropic curves there exists (p. 153) the relation

$$\frac{p_1}{p_4} = \frac{p_3}{p_2} = \left( \frac{T_1}{T_2} \right)^{\frac{n}{n-1}},$$

and therefore it follows that

$$Q_1 = G \left[ c(T_1 - T_2) + ABT_1 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \right]. \quad (45a)$$

and

$$Q_2 = G \left[ c(T_1 - T_2) + ABT_2 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \right], \quad (46a)$$

and accordingly from the formula

$$AL = Q_1 - Q_2$$

we get the work produced in this cycle:

$$L = GB(T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}. \quad (47)$$

In the perfect cycle the work

$$L_m = \frac{Q_1}{AT_1} (T_1 - T_2)$$

is produced, and hence, for the present type of engine and with the help of equation (45a) and of the known relation

$$AB = c_v(\kappa - 1),$$

we can calculate efficiency  $\eta$ :

$$\eta = \frac{c_v(\kappa - 1)(T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}}{c(T_1 - T_2) + c_v(\kappa - 1)T_1 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}}. \quad (48)$$

According to the assumed values of  $n$  and  $c$  there exists here an infinite number of cases; for the particular values  $n=\kappa$  and  $c=0$  we again turn to the C a r n o t cycle.

If the engine is made practical, i.e., d o u b l e - a c t i n g, with  $u$  revolutions per minute and developing a work of  $N$  horse powers, we get, by making use of equation (15), p. 290, in the preceding formula (47), the expression

$$GB(T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} = 30 \times 75 \frac{N}{u}, \quad \left[ = 30 \times 550 \frac{N}{u} \right], \quad (47a)$$

from which can be calculated, for given temperature limits, the weight  $G$  of the air which must be confined in the engine, provided we also assume the pressure ratio  $p_1:p_2$ ; this ratio, to be sure, is arbitrary but must not sink below a particular value. The foregoing formulas only lead to real values when the expression under the logarithmic sign is greater than unity, and therefore the relation

$$\frac{p_1}{p_2} > \left( \frac{T_1}{T_2} \right)^{\frac{n}{n-1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

must be observed throughout. If of the four pressures only one is given, say  $p_1$ , then  $p_2$  will be limited by the chosen value of the preceding pressure ratio, and the other values  $p_3$  and  $p_4$  will be determined from the already used relation

$$\frac{p_1}{p_4} = \frac{p_3}{p_2} = \left( \frac{T_1}{T_2} \right)^{\frac{n}{n-1}}. \quad . \quad . \quad . \quad . \quad . \quad (50)$$

The corresponding volumes then follow from the expression

$$Vp = BGT,$$

provided we substitute the corresponding values of the temperature and pressure belonging to the four vertices of the indicator diagram (Fig. 43a). We then get a measure of the size of the engine cylinder for the case in question, provided that the whole cycle really can be practically carried out in an engine with a single cylinder.

Moreover there will be opportunity below to further elucidate the preceding equations by numerical examples.

The indicator diagram, assumed in Fig. 43*a*, p. 309, is transformed in Fig. 43*b*; for this purpose (see Section I, p. 69) the change of entropy

$$P = G \int \frac{dQ}{AT}$$

is laid off as abscissa from 0 and the temperature  $T$  as ordinate. The transformations of the two isothermal curves  $ab$  and  $cd$  are here given by the horizontals  $a'b'$  and  $c'd'$ , while for the passage from any point of the polytropic curve to any arbitrary temperature value  $T$ , lying between the chosen temperature limits, there is found the change of entropy

$$P = P_0 + \frac{Gc}{A} \log_e T$$

(because  $dQ = GcdT$ ), where  $P_0$  is an arbitrarily chosen constant. This equation represents the transformation  $d'a'$  of the polytropic curve  $da$  (Fig. 43*a*). (Compare p. 159.)

Generally speaking, for the transformation of a point of an indicator diagram, equations (55), p. 135, will hold, provided the mediating body is a gas. If we here use the particular equation (55*c*), in the form

$$AP = AP_0 + c_p \log_e T - (c_p - c_v) \log_e p, \quad . \quad . \quad (51)$$

there will follow, for the change  $ab$ , the length of the portion  $a'b'$  in Fig. 43*b*,

$$a'b' = P_1 P_3 = (c_p - c_v) \log_e \frac{p_1}{p_3},$$

and for the change  $dc$  we get the portion  $d'c'$

$$d'c' = P_4 P_2 = (c_p - c_v) \log_e \frac{p_4}{p_2},$$

and then, because of the relation  $p_1 p_2 = p_3 p_4$ , it results that  $a'b' = c'd'$ ; the transformations of the two poly-

tropic curves  $d'a'$  and  $b'c'$  are therefore horizontally equidistant, in consequence of which the areas under the two curves, hatched in Fig. 43, are equally great, which is a proposition, moreover, that directly follows from the theorems on transformation, because the two hatched areas represent the heat quantities  $Q_1'$  and  $Q_2'$  (Fig. 43, p. 292) measured in units of work, and because there was found above

$$Q_1' = Q_2' = cG(T_1 - T_2).$$

In like manner the two rectangular areas  $a'b'P_3P_1$  and  $d'c'P_2P_4$  represent the heat quantities  $Q_1''$  and  $Q_2''$ , measured in units of work, and the curved quadrilateral  $a'b'c'd'$  represents the produced work  $L$ .

If the curve  $da$  (Fig. 43a) is not polytropic, but any curve whatever, we still can easily construct for this case a second curve  $cb$ , under the assumption that the transformations of the two curves are horizontally equidistant, therefore likewise enclose equal areas.

If, for example,  $T$  is the temperature and  $p$  the pressure for a point of the curve  $da$ , and if for the corresponding point of the curve  $cb$  there exists the same temperature  $T$  but the pressure  $p'$ , then equation (51) will hold for the first point, and for the second

$$AP' = AP_0 + c_p \log_e T - (c_p - c_v) \log_e p';$$

the difference of the two equations is

$$AP - AP' = (c_p - c_v) \log_e \frac{p'}{p},$$

and this value will be the same for all points when

$$\frac{p'}{p} = \text{constant}.$$

If we designate this constant by  $m$ , refer the formulas to the unit of weight of gas, and designate by  $v$  and  $v'$  the volumes which



belong to the corresponding points, we get, for the point of the second curve corresponding to a given point ( $pv$ ), the relations

$$p' = mp \quad \text{and} \quad v' = \frac{v}{m},$$

with which the second curve can easily be constructed from the first.

R a n k i n e<sup>1</sup> calls the two curves, connected in the manner indicated, isodiabatic; according to the preceding investigations the polytropic curves, possessing equal exponents, are at the same time always isodiabatic, i.e., their transformations are horizontally equidistant. These curves play an important rôle in subsequent investigations of the air engines.

## § 55. THEORY OF THE REGENERATOR.

In the cycle represented in Fig. 43, p. 309, there can be computed from equation (45a) the heat quantity  $Q_1$ , which must be supplied on the path  $dab$  to the air existing in the engine:

$$Q_1 = G \left[ c(T_1 - T_2) + ABT_1 \log_e \frac{p_1 \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}}{p_2} \right],$$

and the heat quantity  $Q_2$ , which is to be withdrawn along the path  $bcd$ , is found from equation (46a) to be

$$Q_2 = G \left[ c(T_1 - T_2) + ABT_2 \log_e \frac{p_1 \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}}{p_2} \right].$$

In the first equation, the first term  $Gc(T_1 - T_2)$  represents the quantity of heat which must be supplied for the change  $da$  from one isothermal to the other, and the same term in the second equation, which is likewise  $Gc(T_1 - T_2)$ , represents the quantity of heat which must be withdrawn along the path  $bc$ , i.e., on the return from the second isothermal to the first.

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<sup>1</sup> R a n k i n e, "A Manual of the Steam Engine," 1859, p. 345.

Now if we could regularly store in a body this heat quantity during its return  $bc$ , in order to utilize it again in the subsequent operation along the forward path  $da$ , then, according to both the preceding equations, there would result for the heat quantity  $Q_1$  to be supplied from the outside, i.e., from the heating body, only the amount

$$Q_1 = GABT_1 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}, \dots \dots \dots (52)$$

and for the heat quantity  $Q_2$ , to be given off to the cooling body  $cd$ ,

$$Q_2 = GABT_2 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}, \dots \dots \dots (53)$$

and from this follows the ratio of the two heat quantities,

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \dots \dots \dots (54)$$

But for the cycle before us the work, according to equation (47), is

$$L = GB(T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}. \dots \dots (55)$$

If we divide this expression by equation (52) we get simply

$$L = \frac{Q_1}{AT_1} (T_1 - T_2). \dots \dots \dots (56)$$

Equations (54) and (56) agree exactly with the formulas which have been found for the perfect engine describing a Carnot cycle.

When therefore definite, limiting, temperatures are prescribed for the mediating body (medium) there will exist an infinite number of cycles through which the maxi-

imum of work can be produced, as in the Carnot cycle, provided the two adiabatics of the latter are replaced by any pair of polytropic curves whatever and the possibility of the assumed heat storage exists; yes, the polytropic pair of curves can be of any type whatever, if the two curves are only isodiabatic. (See closing remark in § 54.) But with this all difficulties would disappear which, according to the preceding presentation, p. 291, oppose the practical realization of the Carnot cycle in air engines; the partial removal of these difficulties is in fact rendered technically possible by the application of the regenerator.<sup>1</sup>

Let  $AB$  (Fig. 44) represent the regenerator, i.e., a prismatic vessel which is filled uniformly with a dense weave of wire (which in hot-air engines is replaced by thin or perforated sheets of metal); in the main, it is filled with a body possessing a great surface which can easily absorb and reject heat, and which at the same time offers comparatively little resistance to the passage of the air;

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<sup>1</sup> The regenerator was invented as early as 1816 by Dr. Robert Stirling, and it was not until later that James Stirling and Ericsson made use of it in their hot-air engines. The great importance which the regenerator has attained in other parts of heat technology, through the brothers Wilhelm and Friedrich Siemens, is known to every engineer.

The first theoretical treatment of the question as to the mode of action of the regenerator in hot-air engines is given by Macquorn Rankine ("A Manual of the Steam Engine," 1859, p. 344, etc., and still earlier in "Philosophical Transactions," 1854). Based on these presentations the question is again touched upon by Briot ("Théorie mécanique de la chaleur," Paris, 1869, p. 84, in German by Heinrich Weber, "Lehrbuch der mechanischen Wärmetheorie," Leipzig, 1871, p. 88), also by de Saint Robert ("Principes de Thermodynamique," 2nd Ed., Turin and Florence, 1870, p. 287).

In the second edition of the present book (1866) I did not know of Rankine's presentations, and I erroneously combated the advantage of the regenerator in the air engine because I had only investigated cycles between two adiabatics, for which, to be sure, the uselessness of the regenerator holds. But if, according to Reitlinger, we replace the adiabatics by isothermals, the circumstances change. An enlarged theory of regenerator action is given by J. Hirsch ("Théorie des machines aérothermiques," Annales des ponts et chaussées, 1874, p. 409), and Schröter, making use of the propositions on the transformation of pressure curves, has discussed the question under consideration ("Über die Anwendung von Regeneratoren bei Heisluftmaschinen," Zeitschrift des Vereins deutscher Ingenieure, 1883). The investigations in the present book embrace many additions and applications to specially practical cases.

at the left end  $A$  there is a vessel  $K$  which is filled with air at the lower temperature limit  $T_2$ , and at the right there is a vessel  $H$  which is filled with air at the higher temperature limit  $T_1$ ; suppose a certain quantity of air to have been pushed back and forth several times through the regenerator from the cold to the hot space; then, in the filling of the regenerator, in the wire mesh, there will exist a distribution of temperature whose law is represented by the curve  $CDE$ , provided we lay off  $T$  at any particular place  $P$ , i.e., at the cross-section  $F$  which is at the distance  $AF=OP=x$  from the left end, and lay off at  $P$  the ordinate  $PD=T$  = temperature, above the horizontal axis  $OX$ . In doing this let us assume that the temperature curve is nearly horizontal at its ends, and that therefore the limiting temperatures  $T_2$  and  $T_1$  each extend for a certain distance into the regenerator. Now suppose that again a certain quantity of air has been driven from the cold space  $K$  to the hot space  $H$  through the regenerator, then the air will be brought from the temperature  $T_2$  to  $T_1$ , but simultaneously the temperature curve  $CDE$  will be changed and will now be represented by the curve  $C'D'E'$ ; let us first determine the connection between these two curves.

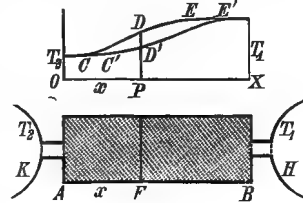


FIG. 44.

Let  $ac$  (Fig. 45) represent the curve element corresponding to point  $D$  of the curve  $CDE$  in Fig. 44; the point  $P$ , whose abscissa is  $x$ , corresponds to the temperature  $T$ , and the point  $Q$  is at the distance  $dx$  from  $P$  and possesses the temperature  $T + dT$ .

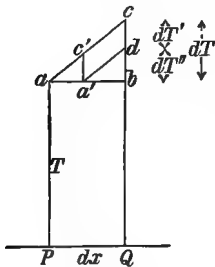


FIG. 45.

Let  $G_0$  be the weight of the filling (wire mesh) of the regenerator per unit of length,  $c_0$  the specific heat of the filling, and  $G$  the weight of air which is forced through the regenerator per second; (we at first suppose a continuous flow of air to take place lasting for some time, and that the regenerator is considerably prolonged to the right;) then the filling  $G_0 dx$ , belonging to the length  $dx$ , must experience a diminution of temperature designated by

$dT''$  and therefore gives off an amount of heat  $dQ$  which is determined by the formula

$$dQ = c_0 G_0 dx dT''.$$

In the corresponding time  $dt$  there passes, through the cross-section  $F$  at the point  $P$ , the weight  $Gdt$  of air which is heated; let the corresponding rise of temperature be  $dT'''$  and the specific heat of the air be  $c$ ; then the quantity of heat which the air has absorbed along the path  $dx$  will be

$$dQ = cGdt \cdot dT'''.$$

By equating the last two expressions we get

$$c_0 G_0 \frac{dx}{dt} dT'' = cGdT'''.$$

But the velocity  $w$  with which the air at the point  $P$  passes the cross-section  $F$  is

$$w = \frac{dx}{dt},$$

hence the preceding formula gives

$$c_0 G_0 w dT'' = cGdT'''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

The two changes of temperature  $dT''$  and  $dT'''$  are represented in Fig. 45 by the distances  $cd$  and  $bd$ , and here we also have

$$dT = dT'' + dT'''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

If through the point  $d$  the line  $da'$  is drawn, parallel to  $ac$  and continued until it cuts the horizontal  $ab$ , then  $a'$  will be that point of the curve  $C'D'E'$  (Fig. 44) which is assumed after an infinitesimal time  $dt$  by the point  $D$  possessing the temperature  $T$ . If we designate the horizontal displacement  $aa'$  (Fig. 45) by  $dx'$ , then, from the similarity of the triangles  $aa'c'$  and  $abc$ , we have the relation

$$\frac{dx'}{dx} = \frac{dT''}{dT}$$

or

$$\frac{dx'}{dt} = \frac{dx}{dt} \frac{dT'}{dT} = v \frac{dT'}{dT}.$$

Now the left member of this equation is nothing but the velocity of the horizontal displacement of the point  $a$  (Fig. 45) or of the point  $D$  of the temperature curve  $CDE$  in Fig. 44; if we designate it by  $u$  there follows

$$u = w \frac{dT'}{dT},$$

and we get, if we eliminate  $dT''$  from the two equations (57) and (58), for this velocity

$$u = \frac{w}{1 + \frac{G_0 c_0}{Gc} w} \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

To be sure the velocity  $w$ , with which the air traverses the different cross-sections of the regenerator, is variable because changes of the volume of the air occur which are due to temperature changes and eventually to the simultaneously occurring pressure changes; strictly speaking, therefore, the velocity  $u$ , with which the different points of the curve  $CDE$  (Fig. 44) progress, is different; but this difference is extraordinarily small, for in the first place the velocity  $w$  of the air in the regenerator is comparatively large, and in the second place the fraction  $\frac{G_0 c_0}{Gc}$ , present in equation (59), always has a very large value; hence in this equation we may unhesitatingly neglect the one (1) in the denominator and then get the much simpler and sufficiently exact relation

$$u = \frac{Gc}{G_0 c_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

and from this derive the proposition that all points of the temperature curve  $CDE$  move with the same velocity. Multiplying both sides of equation (60) by the differential  $dt$  of the time and integrating, there follows

$$s = \frac{Lc}{G_0 c_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (60a)$$

where  $L$  represents the quantity of air in kilograms [pounds] which has been driven through the regenerator in the given time, and  $s$  represents the displacement of the temperature curve thus occasioned; but the two temperature curves  $CDE$  and  $C'D'E'$  (Fig. 44), corresponding to the beginning and the end, are therefore horizontally equidistant in the direction of the axis of the regenerator. The area contained between the two curves will be designated by  $f$  and can be found from

$$f = s(T_1 - T_2) = \frac{Lc}{G_0c_0}(T_1 - T_2)$$

or

$$Q = G_0c_0f, \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

because  $Q = Lc(T_1 - T_2)$  represents the quantity of heat which the air has absorbed in its passage through the regenerator.

Equation (61) may be derived directly as follows. The initial temperature  $T$  in the cross-section  $F$  at the point  $P$  is represented by the ordinate  $PD$ , and at the end it is  $T'$  and represented by the ordinate  $PD'$ ; the part of the regenerator filling  $G_0dx$ , belonging to the length  $dx$ , has therefore experienced a temperature diminution  $T - T'$  and has therefore given off a quantity of heat which is

$$dQ = G_0c_0dx(T - T').$$

Since  $(T - T')dx$  represents the strip of area lying between  $D$  and  $D'$ , integration will give the whole area  $f$ , and the preceding formula will thus also lead to equation (61).

If the air is forced through the regenerator in the reverse direction, a parallel shifting of the curve  $CDE$  takes place in the other direction; consequently if the same quantity of air, after the change of direction, again passes through the regenerator, the curve will return to its original position. To be sure the preceding investigation gives no clue as to the course of the curve itself.

The determination of the quantity of air contained in the regenerator is of importance; it varies, but can be graphically represented for a particular instant and for a particular position

of the temperature curve  $CDE$ . Let  $F$  represent the cross-section of the air-filled portion of the free space of the regenerator at the distance  $x$  from the left end  $A$  (Fig. 44), then  $Fdx$  gives the volume of air for the portion  $dx$  of the length; if  $dG$  is the weight of the air in this space and  $v$  its specific volume there will exist the relation

$$vdG = Fdx.$$

Now multiplying both sides of this equation by the pressure  $p$  of the air, and making use of the equation of condition  $pv = BT$ , we get

$$dG = \frac{Fp}{B} \frac{dx}{T},$$

and this equation can be integrated when we know the course  $T = f(x)$  of the temperature curve  $CDE$  (Fig. 44) of the regenerator, for the pressure  $p$  is everywhere the same. In the lower part of the following figure the temperature curve  $CDE$  of Fig. 44 is represented and repeated; if we designate the reciprocal value of  $T$ , i.e.,  $1/T$ , by  $y$  and lay off  $y$  in the upper part of Fig. 46 as an ordinate  $P'd$ , corresponding to the abscissa  $O'P' = x$ , we get a new curve  $c_0 c d e e_0$ , and integration of the preceding equation gives

$$G_r = \frac{Fp}{B} \int y dx,$$

where  $G_r$  represents the weight of all the air in the regenerator.

This integral is represented by the hatched area of Fig. 46; if we reduce this area to a rectangle having the base  $O'X' = OX = l$ , the axial length of the regenerator, and if  $y_0$  is the height of the rectangle, the preceding equation will give

$$G_r = \frac{F l p y_0}{B}, \quad \dots \dots \dots (62)$$

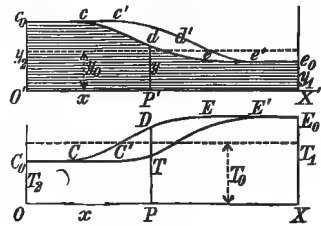


FIG. 46.



or, if we designate the reciprocal value of  $y_0$  by  $T_0$  and remember that  $F'l$  represents the whole space  $V_0$  filled with air, we shall get

$$G_r = \frac{V_0 p}{B T_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62a)$$

where  $T_0$  is a sort of mean temperature in the regenerator; it can also be found directly if we reduce the area  $C_0 C D E E_0$  to a rectangle with the base  $OX = l$ ; the hatched area, however, has the advantage, at once recognized, of showing the law according to which the weight of the air in the regenerator is distributed.

Let us again suppose that  $L$  kg. [lb.] of air are forced from the cold space, through the regenerator, to the hot space, then the parallel displacement  $s$  of the curve  $CDE$  corresponds to an equally great displacement of the curve  $cde$  to  $c'd'e'$ , and the area  $s(y_2 - y_1)$  contained between the two curves expresses the increment of the hatched area (Fig. 46); accordingly, after the passage of the air there will be a larger weight  $G_r'$  of air in the regenerator than it originally contained; and consequently a smaller quantity of air will enter the hot space than was furnished by the cold space,—always assuming that the pressure  $p$  remains constant when the air is passing through.

With the help of equation (62) this difference is found to be

$$G_r' - G_r = \frac{Fp}{B} s(y_2 - y_1),$$

where the displacement  $s$  is given by the equation (60a). The mean ordinate  $y_0$  is increased to  $y_0'$  after the passage of the air, and we have

$$y_0' = y_0 + \frac{s}{l}(y_2 - y_1),$$

from the reciprocal value of which we find the temperature  $T_0'$ , after utilizing equation (60a):

$$T_0' = T_0 \left[ 1 - \frac{Lc}{G_0 l c_0} \frac{T_0(T_1 - T_2)}{T_1 T_2} \right].$$

The second term in the bracket is a very small fraction with hot-air engines. We may therefore assume that the mean temperature in the regenerator only varies between narrow limits, and that the weight  $G$  of the air enclosed in the regenerator is principally dependent upon the pressure  $p$  and nearly proportional to it, according to equation 62a), in so far as the passage of the air through the regenerator is accompanied by any pressure change.

## § 56. CLOSED HOT-AIR ENGINE WITHOUT REGENERATOR.

### First Arrangement (Rider System).

Following the above theoretical investigations of the different cycles of hot-air engines, we will now show how the practical realization of these cycles is possible.

There exists in this direction a whole series of exceedingly ingenious suggestions and constructive efforts, for example by Stirling, by the clever Ericsson, by Laubereau-Schwartzkopf, Rider, Lehmann, and others; with the exception of perhaps Lehmann's engine arrangement, not one of the proposed constructions has been extensively used.

The lack of success is probably partially due to the fact that in the recent suggestions the generator either does not exist at all, or is used in a very imperfect manner; but it may also be due to the fact that real theoretical investigations of the hot-air engines, with a basis of practically possible constructions, do not yet exist. The known investigations are based either on the practically impossible assumption that all parts of the cycle are described in one and the same space, as was assumed in the above developments, or an effort has been made to derive the indicator diagrams for a certain class of engine and thus find the work of the engine; the equally important question as to the quantity of heat which must be supplied to, or withdrawn from, the working air in the constructed engines, during the course of the cycle, has not been answered; the propositions which I have developed on pp. 197 to

225, on the action of the transfer-piston, however, do furnish the means of pursuing the question further.

Let us try to solve the problem of realizing the cycle, represented in Fig. 47, which consists of two isothermals  $T_2T_2$  and  $T_1T_1$  and of the two polytropic curves  $T_2T_1$  and  $T_1T_2$ , and which has already been investigated above, by an engine which can be actually constructed.

Fig. 48a gives a schematic representation of such an engine without a regenerator, an arrangement, moreover, which embraces several cases that have already been proposed and constructed.

Two cylinders  $A$  and  $B$  of the same diameter are separated from each other by a perforated partition  $ab$ .

Piston  $K_1$  moves in cylinder  $A$ , piston  $K_2$  in cylinder  $B$ ; the former cylinder is open at the left, the other at the right, so that atmospheric air acts from the outside on both pistons.

The working quantity of air is included between the two pistons  $K_1$  and  $K_2$ .

A jacket  $C$  surrounds cylinder  $A$ , and through the jacket the heating body (fire gases) flows, so that the air which is in this cylinder, or flows into it, is either kept at the upper temperature limit  $T_1$  or is at once brought to this temperature.

Let the cylinder  $B$ , on the other hand, be provided with a jacket  $D$  through which the cooling body (water) flows, so that the air, existing in this cylinder, is kept at the lower temperature limit  $T_2$ , and the air coming from the hot cylinder  $A$  is immediately cooled to the temperature  $T_2$ . The two cylinder spaces will, in future, be distinguished as *h o t s p a c e* and *c o l d s p a c e*.

Fig. 48b, given under Fig. 48a, represents the piston diagram; the vertical line  $OZ$  represents the time of a full period of the engine which is divided into four parts,  $M$ ,  $N$ ,  $P$ , and  $Z$ .

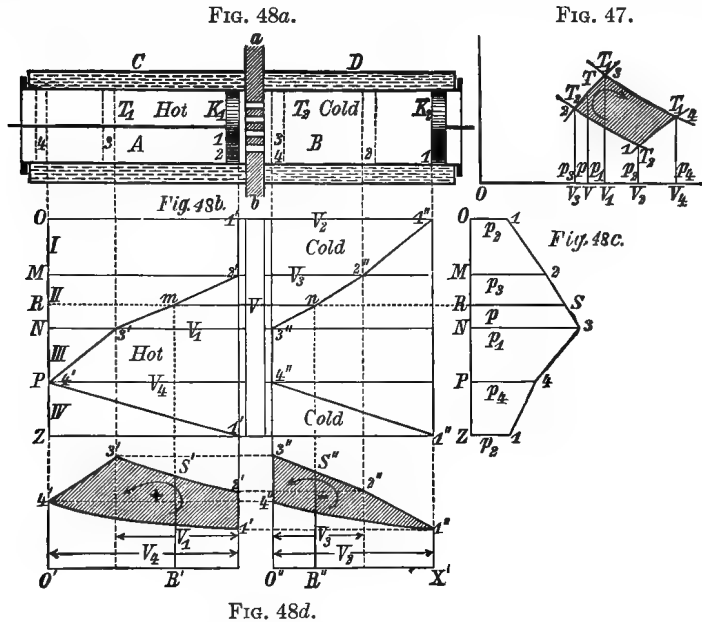
Let us first suppose the pistons  $K_1$  and  $K_2$  to be at the right end of the stroke; at this instant all the air is in the cold space and possesses the volume  $V_2$ , the corresponding pressure  $p_2$ , and the temperature  $T_2$  (see Fig. 47).

The working of the engine is as follows:

In the first time interval  $OM$ , the piston  $K_1$  is held fast and the piston  $K_2$  is shoved from right to left till the air volume

has diminished from  $V_2$  to  $V_3$ ; in so doing the compression takes place at constant temperature  $T_2$  and the pressure grows from  $p_2$  to  $p_3$  (see Fig. 47).

The assumed piston motion is given, in the piston diagram, by the lines  $1''2''$  and  $1'2'$ , and in the adjacent piston force diagram (Fig. 48c) the increase of pressure from  $p_2$  to  $p_3$  is



shown by the portion 12 of the curve corresponding to the time interval  $OM$ .

In the second time interval  $MN$ , both pistons move from right to left; the path of the piston  $K_2$  in the cold space is represented by the displacement curve  $2''3''$ , the air volume  $V_3$  is completely crowded out of the cold space and pushed into the hot space, where the piston  $K_1$  finally limits the volume  $V_1$  of the hot air; line  $2'3'$  (Fig. 48b) is the displacement curve of this piston in the course of the time  $MN$ , within which the pressure of the air grows from  $p_3$  to  $p_1$  according to curve 23 (Fig. 48c).

In the third interval  $NP$ , piston  $K_2$  is held fast (displacement curve is  $3''4''$ ) and piston  $K_1$  travels completely to the left end of

the stroke, as per displacement curve  $3'4'$ ; within this portion of time the air, which is now wholly collected in the hot space, expands under the constant, highest temperature  $T_1$  from the volume  $V_1$  to  $V_4$ , and in so doing its pressure diminishes from  $p_1$  to  $p_4$  according to curve  $34$  (Fig. 48c).

Finally in the fourth time interval  $PZ$  both pistons are brought back from their extreme position on the left to the right end of their stroke; in so doing the whole quantity of air is pushed out of the hot space back into the cold space, the volume  $V_4$  returns to  $V_2$ , the pressure  $p_4$  to  $p_2$ , and thus one period is completed.

In the lower part of the drawing, namely in Fig. 48d, there are exhibited the indicator curves of each of the two cylinders; it is easy to see how these two curves, as well as the piston-force diagram Fig. 48c, can be derived from the given cycle in Fig. 47. According to Fig. 48b, the air volume  $mn = V$  corresponds to the instant of time  $R$ ; if we lay off the distance  $OV$  in Fig. 47 for the volume  $V$ , we shall get in the ordinate  $VT$  the corresponding pressure  $p$ ; this value is laid off at the time point  $R$  (Fig. 48c) as ordinate  $RS$ , and thus gets the corresponding point  $S$  on the curved line of the piston-force diagram.

Finally if we go vertically down to the axis  $O'X'$  (Fig. 48d) from the two points  $m$  and  $n$  (Fig. 48b), and lay off the corresponding pressure  $p$ , we get the two corresponding points  $S'$  and  $S''$  in the two indicator diagrams.

In the engine period described the two indicator diagrams are generated in the direction of the two given arrows; the diagram of the hot space corresponds to positive work, i.e., to the work production of a single cycle, the diagram of the cold space corresponds to negative work, to work consumption. The difference of the two hatched areas gives the whole work delivered by this engine, and this is also measured by the hatched area of the fundamental Fig. 47.

It is worthy of note that the engine cycle just described embraces an infinite number of special cases, for no definite assumption was made as to the twin polytropic curves  $T_2T_1$  and  $T_2T_1$  in Fig. 47.

We easily see that a perfectly definite piston motion in the second and fourth time interval ( $MN$  and  $PZ$  in Fig. 48b) must correspond to a particular value  $n$  of the exponent in the equation of the polytropic curve  $pv^n = \text{constant}$ . For example, if the two displacement curves  $2'3'$  and  $2''3''$  are parallel straight lines, or even horizontally equidistant curves, and if the same is true of  $4'1'$  and  $4''1''$  (Fig. 48b), then the air volume will remain constant both during the transfer from the cold to the hot space, and during the return motion; in this case the polytropic curves  $T_2T_1$  and  $T_2T_1$  are vertical straight lines in Fig. 47, and the cycle of the engine is one which has sometimes been called the Stirling cycle.

In another special case the displacement of the air, from one space into the other and back again, which occurs in the second and fourth time intervals, can be so conducted that the pressure remains constant. In this case the two curves  $T_2T_1$  become horizontal straight lines in Fig. 47, and the engine cycle is one which has been called the Ericsson cycle.

## § 57. CLOSED HOT-AIR ENGINE WITHOUT REGENERATOR.

### Second Arrangement (Lehmann System).

The cycle of a feasible air engine just described can also be realized so far as the assumed cycle is concerned by another engine arrangement. In Fig. 49 let  $AB$  be a cylinder in which two pistons  $K_1$  and  $K_2$  move, of which the former possesses a great length in the horizontal direction, and does not hug the cylinder wall closely in order that the air may spread itself through the remaining annular space; it is called the transfer-piston, while the other piston,  $K_2$ , is called the power-piston.

Let a wall  $ab$ , impenetrable to heat, divide a cylinder externally into two parts. To the left of the wall let the cylinder be surrounded by a jacket  $C$  in which the heating body circulates, and to the right of the wall let the cooling body flow through the jacket  $D$ , and let all this take place in such a way that when the

air is to the left of the transfer-piston  $K_1$  it will be maintained at the upper temperature limit  $T_1$ , while the air to the right, i.e., between the transfer-piston  $K_1$  and the power-piston  $K_2$ , possesses the lower temperature  $T_2$ .

The cycle of Fig. 47 is again represented in the upper part of Fig. 49, and is to be executed by the engine under consideration.

Let the whole time of a period be given by the vertical  $OZ$ ; at the beginning both pistons assume the positions in which they

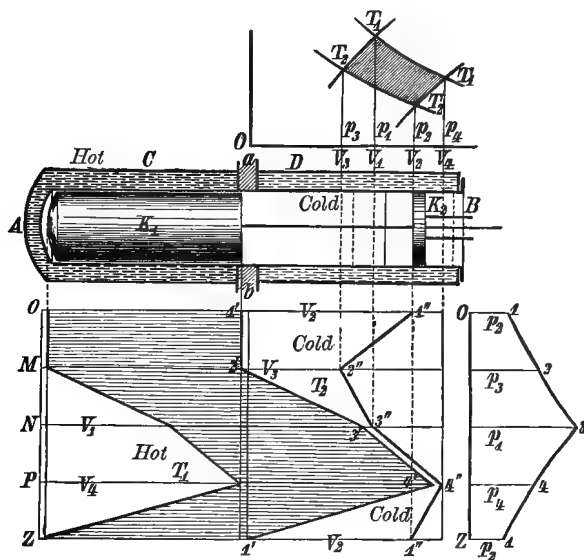


FIG. 49.

are drawn in cylinder  $AB$ . The working of the piston must take place as follows:

**Time interval  $OM$ .** The transfer-piston  $K_1$  is held fast and the piston  $K_2$  is shoved from right to left, so that the air in the cold space is compressed at constant temperature  $T_2$  from the volume  $V_2$  to  $V_3$ , and the pressure grows from pressure  $p_2$  to  $p_3$ . The displacement curves of both pistons are given by the lines  $1'2'$  and  $1''2''$ .

**Time interval  $MN$ .** Both pistons are pushed to the right till they nearly touch each other, the displacement curves in the piston diagram being represented by the lines  $2'3'$  and  $2''3''$ ; in

so doing the total quantity of air is pushed from the cold space into the hot space, which possesses the volume  $V_1$  to the left of transfer-piston  $K_1$ , and its temperature is raised to  $T_1$ ; the pressure has grown from  $p_3$  to  $p_1$ .

Time interval  $NP$ . Both pistons move, nearly touching each other during the whole way, i.e., move together from left to right, the two displacement curves  $3'4'$  and  $3''4''$  being parallel. The air, which is all in the hot space, expands therefore at constant temperature  $T_1$  from the volume  $V_1$  to the volume  $V_4$ , and the pressure sinks from  $p_1$  to  $p_4$ . Finally in the last

Time interval  $PZ$  both pistons move from right to left back to their original positions, whereby the whole quantity of air is driven from the hot space back into the cold space.

It is moreover evident that in the present case, as in the preceding one, the length of the separate time intervals is of no further consequence.

If, for the engine arrangement shown in Fig. 49, we suppose the pipe of an indicator to communicate with the space in which the working air exists, and suppose the indicator drum to be driven by the power-piston  $K_2$ , we shall get directly the indicator diagram (Fig. 49), i.e., the cycle prescribed for the engine. If the indicator drum is connected with the transfer-piston  $K_1$ , there will be obtained an indicator diagram of the form found in Fig. 48*d* for the hot space. The cycle under contemplation also encloses an infinite number of special cases, according to the manner in which the piston is moved in the second and fourth time intervals ( $MN$  and  $PZ$ , Fig. 49).

The engine arrangement discussed corresponds to the general case of *Lehmann's* hot-air engine, while that given in Fig. 48 represents *Rider's* engine working without a regenerator. We see from what has been said that these two kinds of engines do not differ in principle, but only in constructive particulars. In the actually constructed engine of *Rider*, *Lehmann*, and others, the curved lines  $1'2'3'4'1'$  and  $1''2''3''4''1''$  of the piston diagrams (Figs. 48 and 49) are continuously running curves and, indeed, approximately sinusoids, for the pistons are driven by crank mechanisms, a matter to which we will return later.



## § 58. THEORY OF THE ENGINE ARRANGEMENTS JUST DISCUSSED.

The following calculations are simultaneously true for the arrangements given in Fig. 48 and Fig. 49; but the first one will be made the basis of the discussions. As regards the work  $L$  produced by the engine in one period, if we suppose (Fig. 47, p. 325) the cycle to consist of two isothermals and a pair of polytropic curves, then we will have at once equation (47) developed in § 54, p. 310, namely,

$$L = GB(T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}, \dots \dots (63)$$

where  $G$  means the weight of the air enclosed in the engine; at the same time  $n$  is the exponent belonging to the members of the assumed pair of polytropic curves  $T_2T_1$ . However, as regards the quantities of heat  $Q_1$  and  $Q_2$  which must be absorbed or rejected respectively during a period, the two equations (45a) and (46a), p. 310, no longer hold here. We must instead make use of the propositions which were developed in § 38, p. 197, for the action of the transfer-piston.

Here each of the separate time intervals of Fig. 48 must be specially investigated.

In the first interval  $OM$ , air is compressed at constant temperature  $T_2$  from  $V_2$  to  $V_3$ , and the pressure grows from  $p_2$  to  $p_3$ ; the quantity of heat which must, in so doing, be here withdrawn from the air in the cold space, which is designated by  $Q_2'$ , is found from equation (56b) upon p. 137,

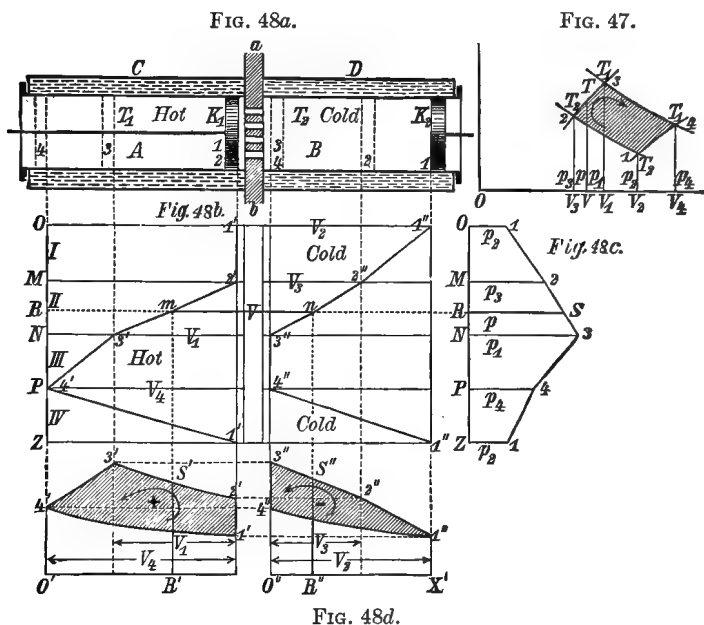
$$Q_2' = ABGT_2 \log_e \frac{p_3}{p_2}, \dots \dots (64)$$

In the third interval all the air in the hot space expands at constant temperature  $T_1$  from the volume  $V_1$  to the volume  $V_4$ , and the pressure sinks from  $p_1$  to  $p_4$ ; the quantity of heat  $Q_1'$

which must hereby be supplied to the hot space, according to the just cited formula, is

$$Q_1' = ABGT_1 \log_e \frac{p_1}{p_4} \dots \dots \dots (65)$$

We must now specially investigate the occurrences in the second interval  $MN$  in which all the air is pushed out of the cold space into the hot space; at the beginning the volume is  $V_3$  and the pressure  $p_3$ ; at the instant of time  $R$  (Fig. 48b) the volume



is  $V$  and the pressure  $p$ , and, in accordance with the hypothesis, the relation

$$pV^n = p_3V_3^n \dots \dots \dots (66)$$

must obtain, where we will for the present avoid making any definite assumptions as to the constant exponent  $n$ . The differentiation of this equation gives

$$Vdp + n p dV = 0 \dots \dots \dots (67)$$

Now we get for the total heat quantity  $Q$  which must be supplied to both spaces, to the hot as well as the cold space, by integration of equation (46), p. 200,

$$dQ = \frac{A}{\kappa - 1} (V dp + \kappa p dV),$$

which, after the utilization of the preceding equation (61), becomes

$$dQ = A \frac{\kappa - n}{\kappa - 1} p dV,$$

and, if besides we determine  $p$  from equation (66), we get the value

$$Q = ABGT_2 \frac{(\kappa - n)}{(\kappa - 1)(n - 1)} \left[ 1 - \left( \frac{V_3}{V_1} \right)^{n-1} \right], \quad . \quad . \quad (68)$$

or, if we substitute the corresponding pressure limit, according to equation (66)

$$Q = ABGT_2 \frac{(\kappa - n)}{(\kappa - 1)(n - 1)} \left[ 1 - \left( \frac{p_1}{p_3} \right)^{\frac{n-1}{n}} \right], \quad . \quad . \quad (68a)$$

and, finally, if we consider the laws concerning the polytropic curve in § 29, p. 153, equation (5),

$$Q = AG \frac{(n - \kappa)}{(\kappa - 1)(n - 1)} B(T_1 - T_2). \quad . \quad . \quad (68b)$$

But this heat quantity  $Q$  is made up of two parts, namely, the one,  $Q_2''$ , which must be supplied to the cold space, and the one,  $Q_1''$ , which is supplied to the hot space.

The first quantity of heat is found by integration of equation (75a), p. 221,

$$Q_2'' = - \int A V_x dp, \quad . \quad . \quad . \quad (69)$$

where  $V_x$  is the instantaneous volume of the air in the discharging space, here the cold space. At the same instant  $R$  of time  $(V - V_x)$  is the volume of the hot space, and therefore, according to equation (42), p. 199, we have the relation

$$\frac{BG}{p} = \frac{V_x}{T_2} + \frac{V - V_x}{T_1}.$$

If we determine  $V_x$  from this and substitute its value, as well as the value of  $V$  proceeding from equation (66), in equation (69), then, by integration and some easily followed transformations, we get for the heat quantity  $Q_2''$ , which must be supplied to the air when it is forced out of the cold space:

$$Q_2'' = ABG \left[ \frac{nT_2}{n-1} - \frac{T_1T_2}{T_1-T_2} \log_e \frac{p_1}{p_3} \right]. \quad (70)$$

On the other hand the quantity of heat  $Q_1''$  which must be imparted to the hot space at the same time is

$$Q_1'' = Q - Q_2'',$$

and, combining preceding equation with equation (68b),

$$Q_1'' = ABG \left[ \frac{(n-\kappa)}{(\kappa-1)(n-1)} T_1 - \frac{\kappa}{\kappa-1} T_2 + \frac{T_1T_2}{T_1-T_2} \log_e \frac{p_1}{p_3} \right]. \quad (71)$$

Finally, in order to determine  $Q_1'''$  and  $Q_2'''$ , which in the fourth time interval  $PZ$  must be imparted to the two spaces, when the air is pushed back from the hot space to the cold space, it is only necessary in the two preceding equations to interchange the temperature values and to substitute the pressures  $p_2$  and  $p_4$  for the pressures  $p_1$  and  $p_3$ ; we then get

$$Q_1''' = ABG \left[ \frac{nT_1}{n-1} - \frac{T_1T_2}{T_1-T_2} \log_e \frac{p_4}{p_2} \right]. \quad (72)$$

and

$$Q_2''' = ABG \left[ \frac{(n-\kappa)}{(\kappa-1)(n-1)} T_2 - \frac{\kappa}{\kappa-1} T_1 + \frac{T_1T_2}{T_1-T_2} \log_e \frac{p_4}{p_2} \right]. \quad (73)$$

Now we finally get the total heat quantity  $Q_1$  which must be imparted by the heating body to the hot space during one engine period, from the relation

$$Q_1 = Q_1' + Q_1'' + Q_1''',$$

and if we here use the preceding formulas and, at the same time, utilize the relations (Fig. 47)

$$\frac{p_1}{p_3} = \frac{p_4}{p_2} \quad \text{and} \quad AB = c_p \frac{\kappa-1}{\kappa}, \quad (74)$$

also substitute

$$\frac{p_1}{p_4} = \frac{p_3}{p_2} = \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}}, \quad . . . . . (75)$$

we get

$$Q_1 = G \left[ c_p (T_1 - T_2) + A B T_1 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \right] . . . (76)$$

Furthermore the quantity of heat  $Q_2$ , which during a whole period must be withdrawn from the cold space, is found from

$$Q_2 = Q_2' - Q_2'' - Q_2''',$$

and from this, with the utilization of the preceding formulas and the several relations last given,

$$Q_2 = G \left[ c_p (T_1 - T_2) + A B T_2 \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \right] . . . (77)$$

The two preceding equations (76) and (77) now conclude the theory of the two engine arrangements given in §§ 56 and 57, pp. 325 and 328, and are distinguished by their great simplicity in spite of the very complicated occurrences involved in the action of the transfer-piston. The difference  $Q_1 - Q_2$  leads again, as it ought, to equation (63), which gives the work  $L$  produced by this engine; but it is interesting that the two expressions, found for  $Q_1$  and  $Q_2$ , for the actually feasible hot-air engines, completely agree in structure with the formulas which were found for the purely theoretical cycle in § 54, p. 310 (equations 45a and 46a). In place of the specific heat

$$c = \frac{n - \kappa}{n - 1} c_v,$$

there corresponding to the polytropic curve employed, we have here in the feasible engine simply the specific heat  $c_p$  of the air under constant pressure; in other respects, however, according to the assumed value of  $n$ , the foregoing propositions hold for an infinite number of cycles, and it is only a question as to the kind of motion of the two pistons  $K_1$  and  $K_2$  (Fig. 48b and 49) in the second and fourth time intervals ( $MN$  and  $PZ$ ). The discussed feasible engines are single-acting; if the engine in question

has  $u$  periods per minute, then its work  $N$  in horse-powers (indicated) according to equation (63) is

$$N = \frac{BG u}{60 \times 75} (T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \quad \dots \quad (78)$$

$$\left[ N = \frac{BG u}{60 \times 550} (T_1 - T_2) \log_e \frac{p_1}{p_2} \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} \right].$$

As the expression under the logarithmic sign must be positive in the preceding equations, the condition

$$\frac{p_1}{p_2} > \left( \frac{T_1}{T_2} \right)^{\frac{n}{n-1}}$$

must be satisfied (see p. 311).

## § 59. APPLICATIONS AND NUMERICAL EXAMPLES.

If we assume that the cycle at the base of the preceding engine arrangements consists of two isothermals and two horizontal straight lines, as indicated in Fig. 50, then we must substitute  $n=0$  in the given equations (this cycle may be called the *Ericsson cycle*, although no *Ericsson engine* ever really described this cycle exactly); let the ratio of the two limiting temperatures  $T_1:T_2$  be designated by  $\lambda$ , then equation (78) gives

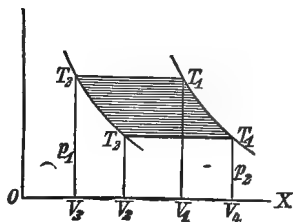


FIG. 50.

$$\frac{N}{u} = \frac{BGT_2}{60 \times 75} (\lambda - 1) \log_e \frac{p_1}{p_2} \quad \dots \quad (78a)$$

$$\left[ \frac{N}{u} = \frac{BGT_2}{60 \times 550} (\lambda - 1) \log_e \frac{p_1}{p_2} \right].$$

On the other hand equations (76) and (77) give the quantities of heat which must be respectively supplied and withdrawn during every engine period:

$$Q_1 = ABGT_2 \left[ \frac{\kappa(\lambda - 1)}{\kappa - 1} + \lambda \log_e \frac{p_1}{p_2} \right], \quad \dots \quad (76a)$$

$$Q_2 = ABGT_2 \left[ \frac{\kappa(\lambda - 1)}{\kappa - 1} + \log_e \frac{p_1}{p_2} \right]. \quad \dots \quad (77a)$$



If the engine makes  $u=100$  revolutions (per minute), and if the lower pressure  $p$ , amounts to just one atmosphere ( $p=10333$  kg. [2116.3 lb.]), we get for  $N=2$  horse powers (indicated)

$$Fs_1=0.025$$

$$[Fs_1=0.8998 \text{ cu. ft.}]$$

If we make the stroke of the transfer-piston  $s_1=0.250$  m. [0.821 ft.], the necessary piston cross-section becomes

$$F=0.100 \text{ qm}$$

$$[F=1.097 \text{ sq. ft.}]$$

and accordingly the diameter is

$$d=0.357 \text{ m.}$$

$$[d=1.1819 \text{ ft.}]$$

On the other hand the stroke of the power-piston, according to equation (81), can be taken  $s_2=0.187$  m. [0.614 ft.].

Under the assumptions made, equation (76b) gives the heat quantity that must here be supplied per minute to the hot space:

$$Q_1=147.72 \text{ cal.}$$

$$[Q_1=594.35 \text{ B.t.u.}]$$

and the heat quantity which must be withdrawn from the cold space in the meantime is

$$Q_2=126.50 \text{ cal.}$$

$$[Q_2=508.97 \text{ B.t.u.}]$$

If the cooling is effected by cold water which, in flowing through the cylinder jacket  $D$  (Fig. 49, p. 328), is heated, say, through  $10^\circ \text{C}$ . [ $18^\circ \text{F}$ .], then the quantity of cooling water necessary per minute is 12.65 kg. [28.28 lb.].<sup>1</sup>

The computed heat quantity  $Q_1$  would give, if the cycle were conducted in a perfect engine describing the Carnot cycle, an amount which expressed in horse powers is

$$N_m = \frac{Q_1}{60 \times 75 A T_1} (T_1 - T_2) = \frac{Q_1}{60 \times 75 A} \frac{(\lambda - 1)}{\lambda},$$

$$[60 \times 550 A T_1] \quad [60 \times 550 A],$$

or, after substituting the corresponding values,

$$N_m=6.959 \text{ horse powers,}$$

$$[N_m=6.86 \text{ horse powers,}]$$

---

<sup>1</sup> For comparison, with observations on a really constructed Lehmann engine, those experimental results will serve which were published by Eckert in the "Technischen Blättern" (Prague, 1869, Vol. I, p. 104). The general agreement of my theoretical results with the dimensions and experimental results there given seems to be a very satisfactory one.



and accordingly the efficiency of this engine, in the formerly given sense, is

$$\eta = \frac{N}{N_m} = 0.287.$$

The two equations (76*b*) and (77*b*) for this efficiency lead to a formula from which we see that it approaches unity more nearly, the larger  $\lambda$  and the pressure ratio  $p_1:p_2$  are taken. In the preceding example the efficiency is very small because the pressure ratio is comparatively small and because the difference of the limiting temperatures is assumed small.

It is moreover worth noting that the Ericsson cycle, assumed in the preceding, gives formulas for the work and for the heat quantities  $Q_1$  and  $Q_2$ , which are identical with those which result from formulas (47), (45*a*), and (46*a*), p. 310, under the supposition that  $c=c_p$  and  $n=0$  for the theoretical cycle assumed in Fig. 43. The identity of these equations with the preceding equations (76), (77), and (78) disappears when the Lehmann engine describes a cycle which is different from the Ericsson cycle.

When we consider the Stirling cycle, that is, when we consider the transfer-piston  $K_1$  (Fig. 49, p. 328) moved in such a way that the displacement of the air takes place at constant volume, and accordingly the contemplated cycle is represented by Fig. 51, then we must substitute  $n=\infty$  in equations (76), (77), and (78). We will here employ the same method of transformation previously used with the Stirling cycle, and again represent the stroke of the transfer-piston by  $s_1$  and the stroke of the power-piston by  $s_2$ . Here

$$V_1 = V_3 \quad \text{and} \quad V_2 = V_4 = Vs_1,$$

and

$$Vs_2 = V_4 - V_2 = V_2 - V_1$$

(see Fig. 49); we also have the relations

$$V_2 p_2 = BGT_2 \quad \text{and} \quad V_1 p_1 = BGT_1.$$

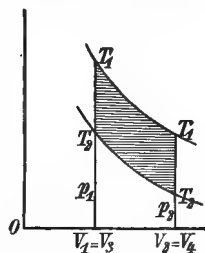


FIG. 51.

From the combination of these equations we get

$$\frac{s_2}{s_1} = 1 - \frac{p_2 T_1^*}{p_1 T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (82)$$

As can easily be seen we furthermore get

$$\frac{N}{u} = \frac{F s_1 p_2}{60 \times 75} (\lambda - 1) \log_e \frac{p_1 T_2}{p_2 T_1}, \quad . \quad . \quad . \quad (78c)$$

[60 × 550]

$$Q_1 = A F s_1 p_1 \left[ \frac{\kappa(\lambda - 1)}{\kappa - 1} + \lambda \log_e \frac{p_1 T_2}{p_2 T_1} \right], \quad . \quad . \quad . \quad (76c)$$

$$Q_2 = A F s_1 p_2 \left[ \frac{\kappa(\lambda - 1)}{\kappa - 1} + \log_e \frac{p_1 T_2}{p_2 T_1} \right], \quad . \quad . \quad . \quad (77c)$$

where both quantities of heat apply to one period.

**Example.** In order to add here also a numerical example, we will assume a *Lehmann* engine which describes the assumed *Stirling* cycle; here again let the temperature ratio  $\lambda = 2$ ; on the other hand let  $p_1 = 4p_2$ , that is, if the lower pressure  $p_2$  is again one atmosphere,  $p_2 = 10333$  kg. [2116.31 lb.], a compression to four atmospheres will take place. If this engine also is to have an indicated performance of  $N = 2$  horse powers with  $u = 100$  periods per minute, we calculate, from equation (78c),

$$F s_1 = 0.0125 \text{ cbm. [0.4414 cu. ft.].}$$

for the space displaced by the transfer-piston per stroke; according to equation (82) for the power-piston the space in question becomes

$$F s_2 = 0.00625 \text{ [0.2207 cu. ft.].}$$

The same values as in the preceding example are obtained for the heat quantities  $Q_1$  and  $Q_2$  and for  $N_m$  and  $\eta$  as well (in consequence of the assumptions here specially made for  $\lambda$ ,  $p_1$ , and  $p_2$ ); this is in accord with the equations (76c) and (77c).

If in these two preceding examples we had substituted the engine arrangement prescribed by Fig. 48 instead of the *Lehmann* arrangement (Fig. 49), then the volume swept through per stroke by the piston  $K_1$  in the hot space would be  $V_4 = F_1 s_1$

and the corresponding volume for the piston in the cold space  $V_2 = F_2 s_2$ , in case the piston cross-sections  $F_1$  and  $F_2$  were different.

According to the propositions concerning the polytropic curve (see Fig. 47, p. 325),

$$\frac{V_4}{V_2} = \left( \frac{T_2}{T_1} \right)^{\frac{1}{n-1}},$$

hence follows

$$F_2 s_2 p_2 = BGT_2$$

and

$$\frac{F_1 s_1}{F_2 s_2} = \left( \frac{T_2}{T_1} \right)^{\frac{1}{n-1}}.$$

If the engine has the *E r i c s s o n* cycle, then  $n=0$ , and therefore the ratio of the two cylinder volumes is

$$\frac{F_1 s_1}{F_2 s_2} = \frac{T_1}{T_2}.$$

When the *S t i r l i n g* cycle is assumed  $n = \infty$ , and therefore

$$F_1 s_1 = F_2 s_2$$

must be assumed. In the actually constructed *R i d e r* engines, which to be sure are provided with a regenerator, the cylinders are in fact of nearly equal capacity.

## § 60. CLOSED HOT-AIR ENGINE WITHOUT REGENERATOR.

### Third Arrangement (L a u b e r e a u - S c h w a r t z - k o p f f System).

Cylinder *AA* (see schematic Fig. 52) is closed at both ends and is divided into two parts by the partition *cd*; the left half is surrounded by a jacket *C* through which the heating body flows, the right half is surrounded by the jacket *D* in which the cooling body (cold water) circulates.

In the cylinder there is a transfer-piston  $K_1$ , whose length is half that of the cylinder; if the piston is at the right

end of its stroke (as in the figure), the whole enclosed air is to the left of the transfer-piston and then has the highest temperature  $T_1$ ; if the transfer-piston  $K_1$  is pushed to the left end, all the air is forced to the right through the annular space between the transfer-piston and the cylinder surface, where it is now brought down to the lower temperature limit  $T_2$ . By suitable heat supply and heat withdrawal on the part of the jacket fluids, the enclosed air, to the left of the transfer-piston, is kept at the temperature  $T_1$ ,

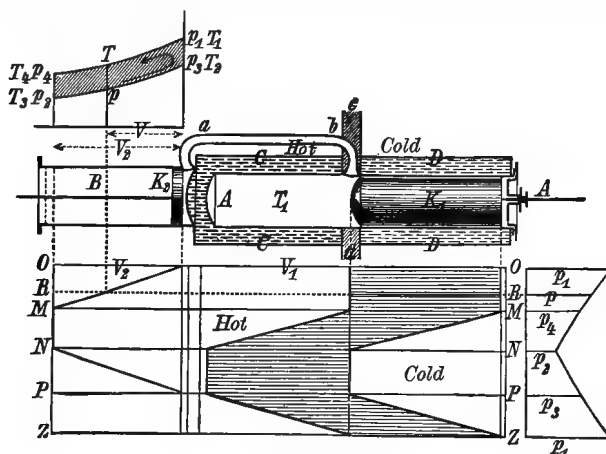


FIG. 52.

and to the right of it, at the temperature  $T_2$ , wherever the transfer-piston may stand.

To the left of cylinder  $AA$  there is a second cylinder  $B$ , the power-cylinder, in which moves the power-piston  $K_2$ ; this cylinder is open on the left so that the atmospheric pressure rests on the left side of the piston  $K_2$ ; on the other hand, the space to the right of piston  $K_2$  is connected with the cylinder  $AA$  by the pipe  $ab$ ; the pipe opens into this cylinder at the middle of its length.

The working of this engine (the normal cycle of the *Laubereau-Schwartzkopff* engine) takes place as follows, provided we take into consideration the lower part of Fig. 52, the piston diagram, and the upper left part of Fig. 52, the corresponding indicator diagram; the time of a period is given by the vertical distance  $OZ$ , and is divided into four parts.

In the beginning both pistons stand at the right end of their stroke, as shown in the figure; all the air weight  $G$  enclosed in the engine (disregarding the clearance space) is here in the hot space, possessing the volume  $V_1$  and the highest pressure  $p_1$ .

In the first time interval  $OM$ , the transfer-piston  $K_1$  is held fast and the piston  $K_2$  is pushed from right to left; in so doing the air expands from the volume  $V_1$  of the hot space to the volume  $V_1 + V_2$ , and indeed the expansion then takes place in the hot space, receiving heat at the constant temperature  $T_1$ , but in the power-cylinder expansion takes place without the absorption or rejection of heat. Here we have before us the special case  $c$  of problem 2, treated in § 39, p. 217, and accordingly there follows from equation (65), p. 217, the equation of the pressure curve  $p_1 p p_4$  (Fig. 52):

$$\frac{p}{p_1} = \left( \frac{\kappa V_1}{\kappa V_1 + V} \right)^\kappa, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (83)$$

and therefore the terminal pressure  $p_4$  of the expansion in the power-cylinder is

$$p_4 = p_1 \left( \frac{\kappa V_1}{\kappa V_1 + V_2} \right)^\kappa \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (84)$$

The work  $L_1$  herewith transmitted to the power-piston is

$$L_1 = \int_0^{V_2} p dV = \frac{\kappa}{\kappa - 1} V_1 p_1 \left[ 1 - \left( \frac{\kappa V_1}{\kappa V_1 + V_2} \right)^{\kappa - 1} \right], \quad \cdot \quad \cdot \quad (85)$$

or, utilizing equation (84),

$$L_1 = \frac{1}{\kappa - 1} [\kappa V_1 (p_1 - p_4) - V_2 p_4]. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (85a)$$

The final temperature  $T_4$  in the power-cylinder is found from the relation

$$G = \frac{V_1 p_1}{B T_1} = \frac{V_1 p_4}{B T_1} + \frac{V_2 p_4}{B T_4},$$

$$\frac{T_4}{T_1} = \frac{V_2 p_4}{V_1 (p_1 - p_4)} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (86)$$

Finally the heat quantity  $Q_1'$ , to be supplied to the hot space in the first time interval, is found from equation (64), p. 217,

$$Q_1' = AV_1(p_1 - p_4). \quad . \quad . \quad . \quad . \quad . \quad . \quad (87)$$

Occurrences in the second time interval  $MN$  (Fig. 52): The power-piston  $K_2$  is held fast at the left end of the stroke, and the transfer-piston  $K_1$  is pushed from right to left; the total volume  $V_1 + V_2$  of the enclosed air herewith remains constant and all the air is forced out of the hot space; in so doing work is neither produced nor consumed, but the pressure sinks from  $p_4$  to  $p_2$  and the temperature of the air in the power-cylinder from  $T_4$  to  $T_3$ .

With this

$$BG = \frac{V_1 p_1}{T_1} = \frac{V_1 p_2}{T_2} + \frac{V_2 p_2}{T_3},$$

from which is found

$$T_3 = \frac{V_2 T_1}{V_1 \left( \frac{p_1}{p_2} - \frac{T_1}{T_2} \right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

During this motion of the transfer-piston, the air is distributed through three spaces; the total volume  $V_1 + V_2$  is invariable, and consequently the heat quantity  $dQ$  which, altogether, at the instant of time  $R$  (Fig. 52), is supplied to the three spaces, is given by equation (46), p. 200:

$$dQ = \frac{A(V_1 + V_2)}{\kappa - 1} dp,$$

or if we integrate, and consider that, during the whole time interval  $MN$ , heat is neither supplied to, nor withdrawn from, the power-cylinder, and also assume that  $Q_1''$  and  $Q_2'$  are the quantities of heat which are respectively supplied to the hot and the cold space, we get

$$Q_1'' + Q_2' = \frac{1}{\kappa - 1} A(V_1 + V_2)(p_2 - p_4). \quad . \quad . \quad . \quad . \quad . \quad . \quad (89)$$

Accordingly this determines the sum of the two quantities of heat; but as regards the determination of the separate heat quantities  $Q_1''$  and  $Q_2'$  we here encounter a problem demanding an essential extension of the theory of the action of the transfer-piston, developed above in § 38. Considering the subordinate importance of this special problem we will only make an approximate determination of these two heat quantities, after we have presented the investigation of the whole cycle.

In the third time interval  $NP$  (Fig. 52), the transfer-piston  $K_1$  is held fast at the left end of its stroke, and the power-piston  $K_2$  is pushed from left to right, and thus the air contained in the power-cylinder  $B$  is brought entirely into the cold space. In so doing the pressure grows according to the curve  $p_2p_3$ , and a certain amount of compression work  $L_2$  is consumed.

Let us designate the variable values of pressure and temperature by  $p$  and  $T$  and consider that here the cylinder  $B$  is the discharging space, and that it receives no heat while the air is being forced out, so that we must substitute  $dQ_x=0$ , and  $T$  in place of  $T_x$ , in equation (47), p. 203, thus getting by integration

$$\frac{T}{T_3} = \left(\frac{p}{p_2}\right)^{\frac{\kappa-1}{\kappa}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (90)$$

and

$$\frac{T_2}{T_3} = \left(\frac{p_3}{p_2}\right)^{\frac{\kappa-1}{\kappa}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

from which can be determined how the temperature varies with the pressure, and what pressure  $p_3$  exists at the end.

If  $V$  is the volume of the air in the power-cylinder at the instant when the pressure  $p$  prevails there, we have the relation

$$BG = \frac{Vp}{T} + \frac{V_1p}{T_2} = \frac{V_1p_3}{T_2}.$$

Combination with the preceding two equations then gives the equation of the compression curve  $p_2p_3$  (Fig. 52)

$$V\left(\frac{p}{p_3}\right)^{\frac{1}{\kappa}} + V_1\left(\frac{p}{p_3}\right) = V_1, \quad . \quad . \quad . \quad . \quad . \quad (92)$$

and then follows, as is easily seen, the compression work

$$L_2 = \int_0^{V_2} p dV$$

$$= V_1 p_3 \left[ \frac{1}{\kappa - 1} \left( 1 - \left( \frac{p_2}{p_3} \right)^{\frac{\kappa - 1}{\kappa}} \right) + \frac{\kappa - 1}{2\kappa - 1} \left( 1 - \left( \frac{p_2}{p_3} \right)^{\frac{2\kappa - 1}{\kappa}} \right) \right]. \quad (93)$$

Now follows the heat quantity  $Q_2''$ , which in this time interval is supplied to the cold space, because no heat is imparted to the power-cylinder during compression, namely, according to equation (46), p. 200,

$$dQ = \frac{A}{\kappa - 1} (V dp + \kappa p dV) = \frac{A}{\kappa - 1} d(Vp) - A p dV,$$

whose integration gives

$$Q_2'' = \frac{A}{\kappa - 1} [V_1 p_3 - (V_1 + V_2) p_2] - A L_2. \quad . \quad . \quad . \quad (94)$$

Finally in the fourth time interval  $PZ$  (Fig. 52) the power-piston  $K_2$  is held fast, and the transfer-piston  $K_1$  is pushed from left to right.

The pressure herewith grows from  $p_3$  to  $p_1$  and the relation

$$BG = \frac{V_1 p_1}{T_1} = \frac{V_1 p_3}{T_2},$$

obtains, according to which

$$p_3 = \frac{T_2}{T_1} p_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (95)$$

The total volume is constant, the external work is zero, and the quantity of heat which is to be supplied to both spaces follows from equation (46), p. 200:

$$Q_1''' + Q_2''' = \frac{A V_1}{\kappa - 1} (p - p_3). \quad . \quad . \quad . \quad . \quad . \quad (96)$$



Here the cold space is the discharging space and therefore, from the propositions on p. 210, the heat which must be imparted to it is

$$Q_2''' = \frac{AV_1}{\lambda-1}(p_1-p_3) - \frac{AV_1p_1}{\lambda-1} \log_e \frac{p_1}{p_3}, \quad . \quad . \quad . \quad (97)$$

if we again designate the temperature ratio  $T_1:T_2$  by  $\lambda$ ; the heat quantity  $Q_1'''$ , which must herewith be supplied to the hot space, can then be found from the combination of equations (96) and (97).

Only the question raised with equation (89), p. 343, is still undecided.

As the hot space is the discharging space in the second time interval  $MN$  (Fig. 52), we can express the heat quantity  $Q_1''$  approximately by equation (52a), p. 210, namely,

$$dQ_1'' = AVdp,$$

where  $V$  is the volume of the hot space at the instant; during the time interval  $MN$  the temperature in the power-cylinder sinks from  $T_4$  to  $T_3$ ; if we assume for this a certain constant mean temperature  $T_0$  there will obtain for the instant of time  $R$

$$BG = \frac{V_2p}{T_0} + \frac{Vp}{T_1} + \frac{(V_1-V)p}{T_2} = \frac{V_1p_1}{T_1}.$$

If we substitute in this formula

$$\frac{T_1}{T_2} = \lambda \quad \text{and} \quad \frac{T_1}{T_0} = \lambda_0,$$

we derive

$$(\lambda-1)V = \lambda_0V_2 + \lambda V_1 - \frac{V_1p_1}{p}.$$

Substitution in the preceding differential formula and the subsequent integration then give an approximate expression for

the heat quantity  $Q_1''$ , which must be supplied to the hot space during the second time interval:

$$Q_1'' = \frac{A(\lambda_0 V_2 + \lambda V_1)}{\lambda - 1} (p_4 - p_2) - \frac{A V_1 p_1}{\lambda - 1} \log_e \frac{p_4}{p_2}, \quad . \quad . \quad (98)$$

and thus there will also be determined, according to equation (89), the heat quantity  $Q_2'$  which must be supplied to the cold space in the assumed time interval.

All the separate formulas are now to be grouped in the following manner. First there results the work  $L$  which is produced by this engine per period,  $L = L_1 - L_2$ , where equations (85a) and (93) come into use; furthermore, the heat quantity  $Q_1$ , which is to be imparted per period to the hot space, is

$$Q_1 = Q_1' + Q_1'' + Q_1''',$$

and the heat quantity to the cold space

$$Q_2 = Q_2' + Q_2'' + Q_2'''.$$

The latter value naturally turns out to be negative, and by change of sign gives the quantity of heat which the cooling body must withdraw from the cold space per period.

The separate terms of the right sides of the equations involved are given above and substitution then gives the relation  $AL = Q_1 - Q_2$ , as it ought; but the substitution leads to very complicated expressions which we will therefore avoid reproducing here; what has been given enables one to follow all the separate phases of the normal cycle of the *L a u b e r e a u - S c h w a r t z k o p f f* engine.

For the sake of completeness I wished to insert the investigation of this engine, although it shows an evident defect, namely, that the hot air during its expansion in the power-cylinder acts on the power-piston, while usually it is a rule (followed also in the *R i d e r* and *L e h m a n n* systems) that the power-piston is exposed to the pressure of the cold air.

The engine, in the form applied by *Schwartzkopff*, has been beautifully thought out and was subjected by *Tresca*<sup>1</sup> to thorough tests; moreover there have subsequently arisen propositions concerning the construction of hot-air engines which in principle return to the arrangement of *Laubereau-Schwartzkopff*; this also may justify us in here investigating this arrangement more fully.

**Numerical Example.** For an engine of the character under consideration the following ratios are given:

$$\frac{T_1}{T_2} = \lambda = 2; \quad \frac{p_1}{p_2} = 4; \quad \frac{V_1}{V_2} = 1.25.$$

Then by Fig. (52) are found from equations (84) and (95):

$$\frac{p_4}{p_1} = 2.1224 \quad \text{and} \quad \frac{p_3}{p_2} = 2.$$

Furthermore, according to equations (86) and (88):

$$\frac{T_4}{T_1} = 0.9044, \quad \frac{T_3}{T_1} = 0.4000.$$

The expansion- and compression-work, according to equation (85a) and (93):

$$L_1 = 2.8946 V_2 p_2; \quad L_2 = 1.4457 V_2 p_2,$$

and therefore the engine work per period is

$$L = L_1 - L_2 = 1.4489 V_2 p_2.$$

The separate heat quantities moreover are:

$$\begin{aligned} Q_1' &= 2.3470 A V_2 p_2, \text{ equation (87),} \\ Q_1'' &= 0.7269 A V_2 p_2, \text{ equation (98),} \\ Q_1''' &= 7.0631 A V_2 p_2, \text{ equations (96) and (97),} \\ Q_2' &= -6.8864 A V_2 p_2, \text{ equations (89) and (98),} \\ Q_2'' &= -0.8360 A V_2 p_2, \text{ equation (94),} \\ Q_2''' &= -0.9657 A V_2 p_2, \text{ equation (97).} \end{aligned}$$

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<sup>1</sup> *Tresca*, "Annales du Conservatoire des arts et métiers," IV, p. 113; *Delabar*, *Dingler's Polytechn. Journal*, 1864, Vol. 172, p. 81.

Accordingly the first three values give for the total heat  $Q_1$ , which must be supplied per period to the h o t space,

$$Q_1 = 10.1370 \, A V_2 p_2.$$

The last three values give the heat quantity  $Q_2$  which must be withdrawn from the c o l d space per period:

$$Q_2 = 8.6881 \, A V_2 p_2.$$

At the end of the expansion in the power-cylinder there prevails there a temperature  $T_3$  which lies even b e l o w the temperature  $T_2$  in the cold space, and indeed here  $T_1 = 0.8 \, T_2$ ; in this cylinder therefore a very considerable lowering of temperature occurs during expansion.

Let us further assume that the engine works between the pressures of 2 and 0.5 atmospheres, consequently  $p = 0.5 \times 10333$  kg. [1008.16 lb.], and the diameter of the power-cylinder  $d = 0.5$  m. [1.64 ft.], and the stroke  $s = 0.40$  m. [1.312 ft.], then calculation gives

$$A V_2 p_2 = 0.9570.$$

From this follows the indicated work per period of the engine

$$\begin{aligned} L &= 588 \text{ mkg.} \\ [L &= 4253 \text{ ft-lb.}] \end{aligned}$$

and the corresponding heat quantities

$$\begin{aligned} Q_1 &= 9.701 \quad \text{and} \quad Q_2 = 8.314 \text{ Cal.} \\ [Q_1 &= 38.497 \quad \text{and} \quad Q_2 = 32.993 \text{ B.t.u.}] \end{aligned}$$

If the engine makes  $u = 36$  revolutions (periods) per minute, then the (indicated) work in horse-powers is

$$\begin{aligned} N &= \frac{Lu}{60 \times 75} = 4.70 \text{ horse power} \\ \left[ N &= \frac{Lu}{60 \times 550} = 4.64 \text{ horse power} \right]. \end{aligned}$$

If the cooling water is heated through  $15^\circ \text{ C.}$  [ $27^\circ \text{ F.}$ ], then the water per minute necessary is 20 kg. [44 lb.] or per hour 1200 l. [about 300 gallons].

Now, to be sure, the above-mentioned experiments by T r e s c a on an engine of the dimensions here assumed gave results which

differed considerably from the preceding, computed, ones; the indicated work was only 0.4 of that here calculated, and the effective performance measured at the brake amounted to only about 0.8 horse-power; the indicator diagrams also have a very different form from that indicated in Fig. 52. To be sure the greatest pressure was 1.45 and the least 0.85 atmospheres, instead of 2 and 0.5 atmospheres as was here assumed.

The deviation is due to the fact that the cycle of the actually constructed engine is far from approaching the normal cycle. We may well say that, on the whole, the separation of the power-cylinder from the heating and cooling space is not to be recommended. Accordingly the Rider and Lehmann arrangement is to be preferred, and for the additional reason that here the regenerator can be employed without difficulty.

## § 61. CLOSED HOT-AIR ENGINE WITH REGENERATOR.

### First Arrangement (Rider System).

The schematic representation of the engine here given in Fig. 53a is only distinguished from that in Fig. 48 by regenerator  $R$  being inserted between the two cylinders  $A$  and  $B$ ; the interior of the regenerator is in free communication with these two spaces  $A$  and  $B$ . The piston diagram, Fig. 53b, the piston-force diagram, Fig. 53d, and the indicator diagram, Fig. 53c, do not differ in general character from the assumed diagrams in Fig. 48.

Let the cycle which the engine before us is to execute be prescribed by the diagram, Fig. 53e, and let it again take place between the two isothermals  $T_1T_1$  and  $T_2T_2$  and the two polytropic curves  $T_2T_1$  and again  $T_2T_1$ , which obey the law

$$pV^n = \text{constant},$$

where  $V$  represents at any instant the combined volumes of the air in the hot space and the cold space (with the exclusion of the volume  $V_0$  of the air in the regenerator).

For the four varieties of the cycle we therefore have the relations

$$p_3 V_3^n = p_1 V_1^n \quad \text{and} \quad p_4 V_4^n = p_2 V_2^n,$$

from which we can also derive

$$\left(\frac{p_3}{p_1}\right)^{\frac{n-1}{n}} = \frac{V_3 p_3}{V_1 p_1} \quad \text{and} \quad \left(\frac{p_4}{p_2}\right)^{\frac{n-1}{n}} = \frac{V_4 p_4}{V_2 p_2} \quad \dots \quad (99)$$

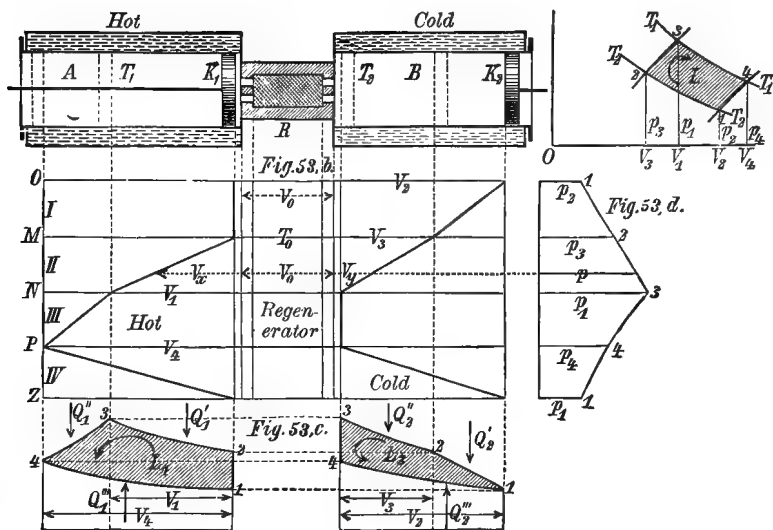


FIG. 53a.

FIG. 53e.

Now, as regards the course of the two isothermals, we get for the point 1 of the first isothermal  $T_2 T_2$  the equation

$$BG = \left( \frac{V_2}{T_2} + \frac{V_0}{T_0} \right) p_2$$

or

$$BGT_2 = \left( 1 + \frac{T_2 V_0}{T V} \right) V_2 p_2,$$

when  $T_0$  represents the mean temperature in the regenerator (in the sense indicated above) at this instant. For any other point of the same isothermal for which  $V$  is the instantaneous

ous volume, and  $p$  the pressure, and for which  $T$  is a corresponding mean temperature in the regenerator, we find

$$BG = \left( \frac{V}{T_2} + \frac{V_0}{T} \right) p_2$$

or

$$BGT_2 = \left( 1 + \frac{T_2}{T} \frac{V_0}{V} \right) Vp.$$

I now set up the hypothesis that during the isothermal changes the mean temperature in the regenerator varies in such a way that the product  $TV$  remains invariable, so that we can write

$$TV = T_0V_2.$$

If, for the sake of simplicity, we make in what follows

$$\frac{T_2V_0}{T_0V_2} = m, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (100)$$

then the last of the preceding equations gives

$$BGT_2 = (1+m)Vp.$$

In the same way, for any point of the second isothermal  $T_1T_1$  we get the relation

$$BGT_1 = (1+\lambda m)Vp$$

when the ratio  $T_1:T_2$  of the limiting temperatures is again represented by  $\lambda$ . For the four vertices of the cycle assumed in Fig. 53e there follow the relations

$$\left. \begin{aligned} BGT_2 &= (1+m)V_2p_2 = (1+m)V_3p_3, \\ \lambda BGT_2 &= (1+\lambda m)V_1p_1 = (1+\lambda m)V_4p_4. \end{aligned} \right\} . \quad . \quad . \quad (101)$$

From this results

$$V_3p_3 = V_2p_2 \quad \text{and} \quad V_4p_4 = V_1p_1, \quad . \quad . \quad . \quad (102)$$

and in combination with equation (99)

$$\frac{p_1}{p_3} = \frac{p_4}{p_2} \quad \text{and} \quad \frac{V_1}{V_3} = \frac{V_4}{V_2}. \quad . \quad . \quad . \quad . \quad (103)$$

If we regard the limiting pressures  $p_1$  and  $p_2$  as given, likewise  $\lambda$  and the value  $m$  according to equation (100), we shall get

$$V_1 = \frac{(1+m)\lambda}{1+m\lambda} \frac{p_2}{p_1} V_2, \quad . \quad . \quad . \quad . \quad . \quad (104)$$

and when the exponent  $n$  of the polytropic curve is given, we can also determine, according to equations (99) and (102), the values  $V_3$  and  $V_4$ ,  $p_3$  and  $p_4$ , as follows:

$$\frac{V_4}{V_2} = \left[ \frac{1+m\lambda}{\lambda(1+m)} \right]^{\frac{1}{n-1}} \quad \text{and} \quad \frac{p_4}{p_2} = \left[ \frac{\lambda(1+m)}{1+m\lambda} \right]^{\frac{n}{n-1}}. \quad (104a)$$

Here  $V_4$  is the volume of the hot cylinder;  $V_3$  and  $p_3$  can be found from equations (103).

The application of the formulas developed and also of the following propositions of course assumes the reliability of the hypothesis just set up, concerning the variability of the temperature in the regenerator; but the assumption made appears to me thoroughly reliable; the variability always falls on the side expected and is always confined between comparatively narrow limits, because it always happens that only a part of the air enclosed in the engine fills the regenerator. At any rate we must take refuge in an hypothesis, for an exact theory of the regenerator, closely fitting the facts, is hardly possible. At the first glance it seems more natural to regard the mean temperature in the regenerator, during the whole course of the cycle, as constant, and this assumption has in fact been made by *Gustav Schmidt*,<sup>1</sup> *Slaby*,<sup>2</sup> and *Schöttler*<sup>3</sup>; but if we test this hypothesis by the propositions developed above on pp. 197 to 225, concerning the action of the transfer-piston, we get the absurd result that the regenerator, during a period of the engine, delivers more heat to the air flowing through it than it has absorbed in the same time

<sup>1</sup> *Gustav Schmidt*, "Theorie der geschlossenen kalorischen Maschinen," *Civilingenieur*, Vol. 8, 1862, p. 285.

<sup>2</sup> *Slaby*, "Beiträge zur Theorie der geschlossenen Luftmaschinen," *Verhandlungen des Vereins zur Beförderung des Gewerbeleisses*, Berlin, 1878.

<sup>3</sup> *Schöttler*, "Über die Heisluftmaschine von *Rider*," *Zeitschrift des Vereins deutscher Ingenieure*, 1881, Vol. 25, p. 633.



in the corresponding part of a period, i.e., has stored up for subsequent utilization. The authors mentioned could not recognize the unreliability of their hypothesis, for they confined themselves to the determination of the engine work and to the investigation of the indicator diagrams; they left out of consideration just the most important part of the problem, namely, the determination of the heat quantities which must be supplied to, and withdrawn from, the engine per period; for up to that time the action of the transfer-piston had not been closely examined.

With the help of the presentations in § 38, p. 197, we can approach the investigation of the cycle described by the engine arrangement assumed in Fig. 53, p. 351; in so doing, however, it will be assumed that the air coming from the regenerator always attains there that temperature which prevails in the space into which the air enters.

(a) *Occurrences in the first time interval (I), Fig. 53.* The piston  $K_1$  is held fast and the piston  $K_2$  is pushed from right to left; at the instant in which the volume of the cold space has decreased from  $V_2$  to  $V$  and for which the pressure is  $p$ , there exists the relation

$$BGT_2 = (1+m)Vp,$$

which was given on p. 352. The work  $L_2'$  during the whole time interval I is therefore found by integrating the equation  $dL_2' = pdV$ , with the help of the preceding formula,

$$L_2' = -\frac{BGT_2}{1+m} \log_e \frac{p_3}{p_2}. \quad . \quad . \quad . \quad . \quad (105)$$

The heat quantity  $Q_2'$  herewith supplied to the cold space  $B$  can be found by integrating the formula:

$$dQ_2' = -AVdp = -Ad(Vp) + ApdV,$$

because the space  $B$  is here the discharging space and a part of the air is forced into the regenerator (see equation (47a), p. 203), in which also  $T_x = T_2$  is constant; hence we get

$$Q_2' = AL_2' + AV_2p_2 - AV_3p_3. \quad . \quad . \quad . \quad . \quad (106)$$

(b) *Occurrences in the second time interval (II).* The piston  $K_2$  goes to the very end of the left stroke and piston  $K_1$  sweeps through the volume  $V_1$  in the hot space; in so doing the air is forced through the regenerator from the cold to the hot space.

At a certain moment when the volume of air in the hot space is  $V_x$ , and in the cold space  $V_y$ , and the mean temperature in the regenerator is  $T$  for the instant, the pressure  $p$  can be found from the relation

$$BG = \left( \frac{V_x}{T_1} + \frac{V_y}{T_2} + \frac{V_0}{T} \right) p.$$

If we make  $V_x + V_y = V$  and corresponding to our hypothesis  $VT = V_2T_0$ , there will follow, with the use of equation (100),

$$V_x - \frac{\lambda(1+m)}{\lambda-1} V = -\frac{\lambda}{\lambda-1} \frac{BGT_2}{p},$$

and from this, provided we differentiate and multiply by  $p$ ,

$$pdV_x = -\frac{\lambda}{\lambda-1} BGT_2 \frac{dp}{p} + \frac{\lambda(1+m)}{\lambda-1} pdV.$$

But in general we have for the polytropic curve (p. 152)

$$pdV = -\frac{1}{n-1} d(Vp),$$

and because

$$pdV_y = pdV - pdV_x$$

there follows

$$pdV_x = -\frac{\lambda}{\lambda-1} BGT_2 \frac{dp}{p} - \frac{\lambda(1+m)}{(\lambda-1)(n-1)} d(Vp) \quad . \quad (107a)$$

and

$$pdV_y = +\frac{\lambda}{\lambda-1} BGT_2 \frac{dp}{p} + \frac{1+m\lambda}{(\lambda-1)(n-1)} d(Vp). \quad . \quad (108a)$$

Integration of the first equation gives the work  $L_1'$ , and integration of the other equation the work  $L_2''$ , which is respectively produced in the hot space and in the cold space:

$$L_1' = -\frac{\lambda}{\lambda-1} BGT_2 \log_e \frac{p_1}{p_3} - \frac{\lambda(1+m)}{(\lambda-1)(n-1)} (V_1 p_1 - V_3 p_3), \quad (107)$$

$$L_2'' = +\frac{\lambda}{\lambda-1} BGT_2 \log_e \frac{p_1}{p_3} + \frac{1+m\lambda}{(\lambda-1)(n-1)} (V_1 p_1 - V_3 p_3). \quad (108)$$

Here the hot space is the discharging space, for which equation (46a), p. 202, will give the heat  $dQ'$  to be imparted, and we must there substitute  $T_x = T_y = T_1$  because the air coming from the regenerator already possesses the temperature  $T_1$ ; therefore

$$dQ' = -AV_x dp = -Ad(V_x p) + A p dV_x. \quad (109a)$$

The heat quantity  $dQ''$  for the discharging space is, according to equation (47a), p. 203,

$$dQ'' = -AV_y dp = -Ad(V_y p) + A p dV_y. \quad (110a)$$

The integration of the first equation gives the quantity of heat  $Q_1'$  for the hot space, and the second equation the heat quantity  $Q_2''$  which must be supplied to the cold space:

$$Q_1' = AL_1' - AV_1 p_1. \quad (109)$$

and

$$Q_2'' = AL_2'' + AV_3 p_3. \quad (110)$$

(c) *Occurrences in the third time interval (III), Fig. 53, p. 351.* Here the piston  $K_2$  stands at the left end of its stroke, piston  $K_1$  goes completely to the left end of the stroke.

If  $p$  is the pressure and  $V$  the variable volume of the hot space, then according to p. 343 there will obtain the relation

$$\lambda BGT_2 = (1 + \lambda m) V p.$$

The produced work  $L_1''$  is found by integrating the equation for  $p dV$ , and the heat quantity  $Q_1''$  by integrating the expression

$$-AV dp = -Ad(Vp) + A p dV.$$

Utilizing the preceding relation there follows

$$L_1'' = \frac{\lambda}{1+\lambda m} BGT_2 \log_e \frac{p_1}{p_4} \quad . \quad . \quad . \quad . \quad (111)$$

and

$$Q_1'' = AL_1'' + A(V_1 p_1 - V_4 p_4). \quad . \quad . \quad . \quad (112)$$

(d) *Occurrences in the fourth time interval (IV)*, Fig. 53. Both pistons go back from the left to the right end of the stroke; the quantities of work can evidently be determined by the integration of the two equations (107a) and (108a). We get for the work  $L_1'''$  in the hot space

$$L_1''' = -\frac{\lambda}{\lambda-1} BGT_2 \log_e \frac{p_2}{p_4} - \frac{\lambda(1+m)}{(\lambda-1)(n-1)} (V_2 p_2 - V_4 p_4), \quad (113)$$

and for the work  $L_2'''$  in the cold space

$$L_2''' = +\frac{\lambda}{\lambda-1} BGT_2 \log_e \frac{p_2}{p_4} + \frac{1+m\lambda}{(\lambda-1)(n-1)} (V_2 p_2 - V_4 p_4), \quad (114)$$

and finally the heat quantities  $Q_1'''$  and  $Q_2'''$  are determined by the integration of equations (109a) and (110a):

$$Q_1''' = AL_1''' + AV_4 p_4 \quad . \quad . \quad . \quad . \quad (115)$$

and

$$Q_2''' = AL_2''' - AV_2 p_2. \quad . \quad . \quad . \quad . \quad (116)$$

With the help of the preceding formulas, which embrace an infinite number of special cases according to the values assumed for  $n$ , the main questions can now be answered.

The whole work  $L_1$ , which can be produced in the hot cylinder during one period, is found from the expression

$$L_1 = L_1' + L_1'' + L_1''',$$

and the work  $L_2$ , which is consumed in the cold cylinder, is given by

$$L_2 = L_2' + L_2'' + L_2'''.$$

If in the last equation but one we utilize equations (107), (111), and (113), and utilize in the last equation formulas (105), (108), and (114), and consider besides the relation (101) to (104), pp. 352 and 353, we obtain the remarkably simple formulas

$$L_1 = V_1 p_1 \log_e \frac{p_1}{p_4}$$

and

$$L_2 = V_2 p_2 \log_e \frac{p_3}{p_2}.$$

If in addition we employ equation (104) and consider the relation  $p_3 p_4 = p_1 p_2$  from equation (103), we also have

$$L_1 = \frac{\lambda(1+m)}{1+\lambda m} V_2 p_2 \log_e \frac{p_1}{p_4}, \quad . \quad . \quad . \quad . \quad . \quad (117)$$

$$L_2 = V_2 p_2 \log_e \frac{p_1}{p_4}. \quad . \quad . \quad . \quad . \quad . \quad (118)$$

The difference of the two values gives the work  $L$  of the engine per period

$$L = \frac{\lambda-1}{1+m} V_2 p_2 \log_e \frac{p_1}{p_4}, \quad . \quad . \quad . \quad . \quad . \quad (119)$$

in which, with the help of equation (104a),  $p_4$  is determined:

$$p_4 = p_2 \left( \frac{\lambda(1+m)}{1+\lambda m} \right)^{\frac{n}{n-1}}, \quad . \quad . \quad . \quad . \quad . \quad (120)$$

and the auxiliary quantity  $m$  is to be chosen in accordance with equation (100).

Now, as regards the important question of the heat quantities, we can find the quantity of heat  $Q_1$  which is to be imparted to the hot space per period from the expression

$$Q_1 = Q_1' + Q_1'' + Q_1''',$$

and the quantity of heat  $Q_2$ , which is to be withdrawn from the cold space, is given by

$$Q_2 = Q_2' + Q_2'' + Q_2''',$$

if we substitute in the first expression equations (109), (112), and (115), and in the last expression use equations (106), (110), and (116), we get the surprisingly simple propositions

$$Q_1 = AL_1 \quad \text{and} \quad Q_2 = AL_2,$$

where  $L_1$  and  $L_2$  are determined by equations (117) and (118). From the foregoing follow the ratios

$$\frac{L_1}{L_2} = \frac{\lambda(1+m)}{1+\lambda m}, \quad \frac{L_1}{L} = \frac{\lambda(1+m)}{\lambda-1}, \quad \frac{L_2}{L} = \frac{1+\lambda m}{\lambda-1}, \quad \cdot \quad (122)$$

and

$$\frac{Q_2}{Q_1} = \frac{1+\lambda m}{\lambda(1+m)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (123)$$

also

$$\frac{AL}{Q_1} = \frac{\lambda-1}{\lambda(1+m)}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (124)$$

If the same heat quantity  $Q_1$  were utilized in a theoretically perfect engine, the work  $L_m$  would have to be estimated from equation

$$\frac{AL_m}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{\lambda-1}{\lambda};$$

accordingly, by dividing the last two formulas there follows the efficiency for the here investigated hot-air engine,

$$\eta = \frac{L}{L_m} = \frac{1}{1+m}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (125)$$

The quantity  $m$ , according to equation (100), is directly proportional to the air capacity  $V_0$  of the regenerator; therefore if the metallic filling, or the wire mesh, is so dense in the regenerator that its air capacity  $V_0$  can be neglected as too small, then, in all the preceding formulas, we must substitute  $m=0$ ; but then we get exactly the same formulas as were found before when considering the purely theoretical cycle on p. 288; the hot-air engine, with a regenerator of the assumed arrangement, there-

fore approaches more closely the perfect engine in its action, the smaller the volume  $V_0$  of the air confined in the regenerator; we see from this that this air volume, as was to be expected, has exactly the action of a hurtful space (clearance), and that the whole advantage of the regenerator disappears for a particular size of this space.

Therefore these practical rules result:

1. Hot-air engines are always to be provided with a regenerator;
2. the free (air) space  $V_0$  of the regenerator is to be kept as small as possible, relatively to the capacity of the cylinder.

Since the assumed regenerator action demands a certain, and not too small, volume of metallic filling, we must be sure that its intermediate spaces are kept as small as possible. Definite experiences on this point are not recorded, for just those systems of hot-air engines which are in vogue possess no regenerator, except the *Rider* engine. I only know of observations on the regenerator of hot-air engines, from some remarks of *Combes* (*Moniteur industriel*, 1853, No. 1788), that experiments in Havre showed that the resistance offered by the wire mesh in the regenerator to the passage of the air was extraordinarily small, and that the action of the regenerator was almost perfect. The cold air passing through the regenerator was brought almost completely to the upper temperature, and the air on its return gave its heat back completely to the regenerator, the engine in so doing making 50 periods per minute.

The theoretical investigations presented above speak for the view that success may be expected in the construction of hot-air engines with the regenerator. It will therefore be appropriate to illustrate more fully the propositions established by numerical examples.

## § 62. CLOSED HOT-AIR ENGINES WITH REGENERATOR.

## Second Arrangement.

Before we enter into the special investigation just mentioned, let us discuss an engine arrangement describing exactly the same cycle as the one before subjected to discussion in Fig. 53, p. 351.

Fig. 54 is a schematic representation of the engine in question, which we recognize as identical with the *Lehmann* engine, Fig. 49, p. 328, only it has this modification that the transfer-piston  $K_1$  is hollow, and its cavity is filled with wire mesh, thus constituting the regenerator  $R$ , through which the air flows when the transfer-piston is shifted, because the interior of the regenerator is in free communication with both ends of the cylinder.

Concerning the working cycle of the engine and the piston motion, there holds here what was already said in § 57 when considering Fig. 49, p. 328. The idea of putting the regenerator into the interior of the transfer-piston is due to Dr. *Robert Stirling*; but the engine proposed by him (1832) had a special power-cylinder like the *Laubereau-Schwartzkopff* (Fig. 52, p. 341); the latter is therefore identical in principle with the *Stirling* engine, only with the difference that the regenerator is left out.<sup>1</sup>

The engine sketched in Fig. 54 has not been built so far as I know; if the introduction of the regenerator is an improvement, as was proved above to be really the case to the highest degree, then an attempt at practical construction is to be recommended.

Let us now enter upon the special investigation promised; the results of the calculations will simultaneously hold for both the engine arrangements Fig. 53 and Fig. 54.

*Special case 1.* A hot-air engine with a regenerator, with the arrangement shown in Fig. 53 or Fig. 54, is supposed to describe the *Ericsson* cycle, and therefore the cycle given in Fig. 50, p. 335, is taken as a basis. Here the curve portions 1-4 and

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<sup>1</sup> Compare *Civilingenieur*, Vol. I, 1854, p. 92, Table 11, Fig. 1.



2-3 are horizontal straight lines in the indicator diagrams, Figs. 53 and 54; therefore we must put

$$p_3 = p_1, \quad p_4 = p_2, \quad \text{and} \quad n = 0.$$

Concerning the limiting values of the temperatures and of the pressures, we assume the following:

$$\lambda = \frac{T_1}{T_2} = 2 \quad \text{and} \quad \frac{p_1}{p_2} = 2.5.$$

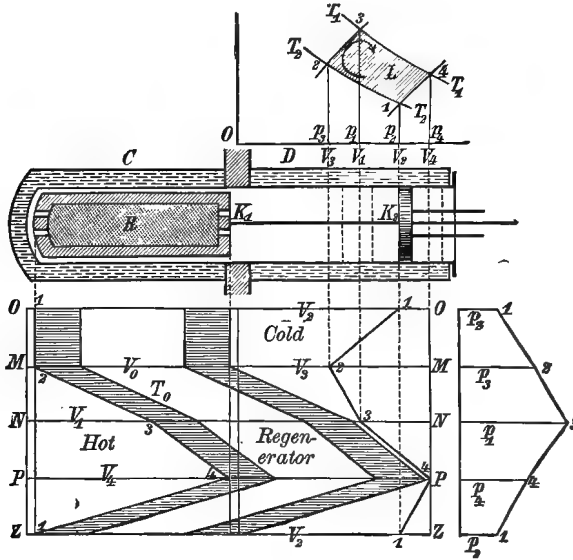


FIG. 54.

Furthermore let the regenerator volume  $V_0 = 0.7 V_2$  and the mean temperature  $T_0$  of the air in the regenerator at the initial position, i.e., when all the air is crowded into the cold space and regenerator, has the value

$$T_0 = \sqrt{T_1 T_2} = T_2 \sqrt{\lambda} = 1.414 T_2;$$

then, according to equation (100), the auxiliary quantity  $m$  becomes

$$m = \frac{V_0 T_2}{V_2 T_0} = 0.495.$$

Now according to equation (119) we have for the work  $L$  of the engine per period,

$$L = 0.4600 V_2 p_2.$$

If we assume the *R i d e r* arrangement, Fig. 53, then, according to equations (122), the indicated work in the hot and cold cylinders respectively will be

$$L_1 = 1.3754 V_2 p_2; \quad L_2 = 0.9154 V_2 p_2.$$

If we substitute the lower pressure  $p_2 = 10333$  kg. [2116.3 lb.], i.e., o n e atmosphere, there follows

$$L = 4753 V_2 \quad [L = 973.5 V_2],$$

and the heat quantities per period:

$$\begin{aligned} Q_1 &= 33.518 V_2 \quad \text{and} \quad Q_2 = 22.301 V_2 \\ [Q_1 &= 3.7664 V_2 \quad \text{and} \quad Q_2 = 2.5067 V_2]. \end{aligned}$$

The efficiency of this engine, according to equation (125), is

$$\eta = 0.669.$$

Moreover we find from equations (104) and (102)

$$V_1 = 0.6010 V_2, \quad V_3 = 0.4000 V_2, \quad \text{and} \quad V_4 = 1.5025 V_2.$$

If both pistons have the same cross-section  $F$ , if  $s_1$  is the stroke of the piston in the hot space, and  $s_2$  for the *R i d e r* arrangement, Fig. 53, the stroke of the piston in the cold space, then because  $V_4 = F s_1$  and  $V_2 = F s_2$  we have from the preceding

$$s_2 = 0.665 s_1.$$

In the *L e h m a n n* arrangement (Fig. 54) the volume described by the piston in the cold space (power-piston) is  $F s_2 = V_4 - V_3 = 1.1025 V_2$ , from which we get

$$s_2 = 0.734 s_1.$$

If this engine had no regenerator, it would, according to equations (65) and (76), pp. 331 and 334, for an equal value of  $\lambda$  and

$p_1:p_2$ , only possess an efficiency  $\eta=0.347$ , so that here the advantage of the regenerator is measurable and stands forth distinctly.

*Special case 2.* A hot-air engine with a regenerator of the arrangement Figs. 53 and 54, describes a Stirling cycle and therefore the cycle given in Fig. 51, p. 338, is taken as a base; here we make  $V_3=V_1$ ,  $V_4=V_2$ , and  $n=\infty$ , and from equation (102) we get the intermediate pressures

$$p_3 = \frac{V_2}{V_1} p_2 \quad \text{and} \quad p_4 = \frac{V_1}{V_2} p_1,$$

and  $V_1$  again follows from equation (104).

If we assume, as in the preceding case,

$$\lambda=2, \quad \frac{p_1}{p_2}=2.5, \quad \text{and} \quad m=0.495,$$

for the present cycle, we again have

$$V_1=0.6010 V_2,$$

and in like manner the work quantities  $L_1$ ,  $L_2$ , and  $L$ , the heat quantities  $Q_1$  and  $Q_2$ , as well as the efficiency, are of the same magnitude. The intermediate pressures are found to be

$$p_3=1.664 p_2 \quad \text{and} \quad p_4=1.502 p_2.$$

If we assume the same cross-section  $F$  for both pistons, and let  $s_1$  be the stroke of the piston in the hot space, and  $s_2$  that of the piston in the cold space, then with the Rider arrangement we have

$$s_2=s_1,$$

because  $V_4$  and  $V_2$  are equal, and represent the spaces swept through by the pistons per period.

On the other hand, if the Lehmann arrangement (Fig. 54) is taken as a base, then the space which is swept through by the power-piston per stroke is

$$F s_2 = V_4 - V_3,$$

from which follows

$$s_2 = 0.299 s_1.$$

The practical construction of the Rider engine in fact shows  $V_4 = V_2$  and  $s_2 = s_1$  approximately; it would also describe the Stirling cycle if its piston motion were that assumed in Fig. 53.

If for such an engine the diameter of each of the two pistons is  $d = 250$  mm. [10 in.] and the stroke of each of the two pistons is  $s_1 = s_2 = 300$  mm. [12 in.], and if moreover the limiting pressures are  $p_2 = 10333$  kg. [2116.3 lb.] and  $p_1 = 2.5 p_2 = 25833$  kg. [5290 lb.], and if the engine makes per minute  $u = 140$  periods (revolutions), then, if  $N$  represents the indicated work in horse powers, we get the relation

$$60 \times 75 N = Lu \quad [60 \times 550 N = Lu],$$

and therefore if in the preceding example we utilize  $L = 4753 V_2$  [ $L = 973.5 V_2$ ] and substitute

$$V_2 = \frac{\pi d^2}{4} s_2 = 0.014726 \text{ cbm. } [V_2 = 0.52006 \text{ cu. ft.}]$$

we get for the work of the engine in horse powers

$$N = 2.177 \quad [N = 2.148].$$

The heat quantities per period follow from the calculated results of the preceding example:

$$\begin{aligned} Q_1 &= 0.4936 \text{ Cal.} & \text{and} & & Q_2 &= 0.3285 \text{ Cal.} \\ [Q_1 &= 1.9588 \text{ B.t.u.} & \text{and} & & Q_2 &= 1.3036 \text{ B.t.u.}] \end{aligned}$$

The quantity of heat which must therefore be withdrawn per hour from the cold space is given by  $60 Q_2 u$ , and consequently the quantity of cooling water needed hourly, if it is heated through  $10^\circ \text{ C.}$  [ $18^\circ \text{ F.}$ ], is given by

$$276 \text{ kg. } [608.35 \text{ lb.}]$$

The found values are of course theoretical ones, because they were found by neglecting the clearance spaces and all other losses of work, and by assuming complete action of the regenerator.

### § 63. HOT-AIR ENGINE WITH A REGENERATOR, AND WITH CONTINUOUS PISTON MOTION GENERATED BY CRANKS.

The kind of piston-motion assumed for the investigations connected with Figs. 48 to 54 rendered possible very different cycles for one and the same engine arrangement, according to the choice of the polytropic curve in question; but the assumed piston motion is not employed in the actually constructed engines; instead of a jerky, discontinuous, motion there are employed motions which are attainable by cranks, occasionally modified by intermediate leverage. We will therefore more fully discuss the hot-air engines, and particularly the *Rider* and *Lehmann* engines, under the hypothesis that they are provided with the regenerator, and that each of the two pistons is moved by a crank, but, for the sake of simplicity, it is assumed that very long connecting-rods are used.

First the *Rider* engine.

Here the two lines which prescribe the law of piston-motion in the piston diagram, Fig. 53, p. 351, are represented by sinusoids.

Let  $V_1$  be the volume swept through by the piston in the hot space,  $V_2$  that for the piston in the cold space, and  $V_0$  the air volume in the regenerator. Lay off (Fig. 55) the values  $V_1$ ,  $V_0$ , and  $V_2$  on a straight line; bisect the distances  $V_1$  and  $V_2$  at the points  $O_1$  and  $O_2$  respectively; with these points as centers describe semicircles with the radii  $O_1R_1 = \frac{1}{2} V_1$ , and  $O_2R_2 = \frac{1}{2} V_2$ , then these radii can be regarded as the corresponding crank radii.

If the piston in the hot space stands at the right end of the stroke in the beginning, then its crank  $O_1R_1$  will be at the right dead-center; but at this instant the crank  $O_2R_2$  of the piston in the cold space may already be at a given angular distance  $\delta$  (in the figure  $\delta = 90^\circ$  is assumed) from its own right dead point; in short, let  $\delta$  be the angle of advance of the crank  $O_2R_2$  relatively to the crank  $O_1R_1$ , the direction of motion of the two cranks being determined by the given arrows. In place of the time for a full period, and for a part of it, we can substitute on the vertical

$OZ$  the angle of turning (crank angle)  $\omega$ , through which both cranks have moved from their initial position; for a full turn we must substitute  $2\pi = OZ$  for  $\omega$ .

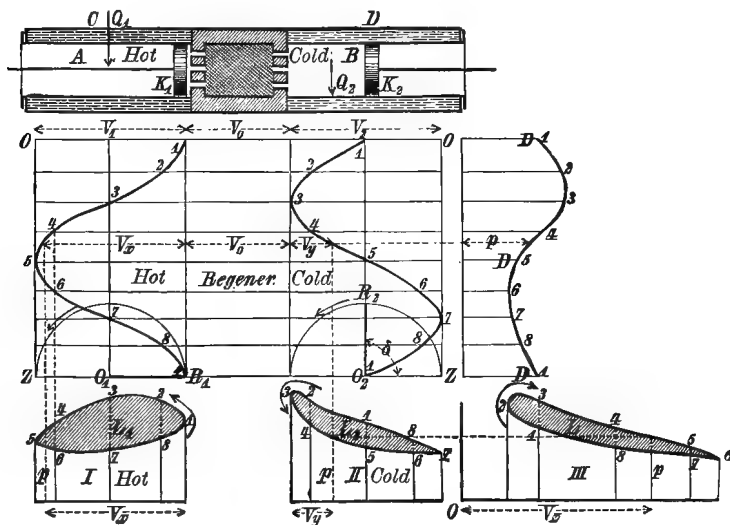


FIG. 55.

There is now no difficulty in determining, for a turning angle  $\omega$  of the cranks, the corresponding volume  $V_x$  of the air in the hot space, and the instantaneous volume  $V_y$  of the air in the cold space; we get at once

$$V_x = \frac{1}{2} V_1 (1 - \cos \omega) \quad . \quad . \quad . \quad (126)$$

and

$$V_y = \frac{1}{2} V_2 [1 + \cos (\omega + \delta)], \quad . \quad . \quad . \quad (127)$$

and accordingly for the crank angle  $\omega$  we get the corresponding total volume of the air in the engine and, designating it by  $V_z$ , write it  $V_z = V_0 + V_x + V_y$ .

If  $G$  is again the weight of the air enclosed in the engine,  $T_1$  the temperature in the hot space,  $T_2$  that in the cold space, and  $T$  the instantaneous mean temperature in the regenerator, in the sense given above, then we have the relation

$$BG = \left( \frac{V_x}{T_1} + \frac{V_y}{T_2} + \frac{V_0}{T} \right) p,$$

where  $p$  is the instantaneous pressure of the air.

Again represent the temperature ratio  $T_1:T_2$  by  $\lambda$  and substitute  $V = V_x + V_y$ , then

$$BGT_2 = \left[ \frac{V_x}{\lambda} + V_y + \frac{V_0 T_2}{VT} (V_x + V_y) \right] p. \quad (128)$$

I now start from the hypothesis that the mean temperature in the regenerator varies, according to the law  $VT = \text{constant}$ , and therefore we may write

$$\frac{V_0 T_2}{VT} = m,$$

where  $m$ , for the engine in question, can be regarded as a given, constant quantity which can be determined with sufficient accuracy by assuming that the mean temperature is  $\sqrt{T_1 T_2} = T_2 \sqrt{\lambda}$ , corresponding to the mean value of  $V_z$ ; therefore, according to equations (126) and (127), we assume

$$VT = V_0 + \frac{V_1 + V_2}{2} T_2 \sqrt{\lambda}$$

and thus determine  $m$ .

From equation (128) we get

$$\frac{\lambda BGT_2}{p} = (1 + m\lambda)V_x + \lambda(1 + m)V_y. \quad (129)$$

Differentiating this expression and then multiplying it on both sides by  $p$  we get

$$-\lambda BGT_2 \frac{dp}{p} = (1 + \lambda m)p dV_x + \lambda(1 + m)p dV_y.$$

We integrate the expression for a full turn and substitute

$$L_1 = \int p dV_x \quad \text{and} \quad L_2 = \int p dV_y,$$

where  $L_1$  represents the total work produced in the hot cylinder and  $L_2$  that in the cold cylinder, which work moreover is given by the indicator diagrams I and II, Fig. 55. As the pressure has one and the same value for the two limits of integration, it follows from the last equation that

$$(1 + m\lambda)L_1 + \lambda(1 + m)L_2 = 0.$$

Furthermore the whole work  $L$ , produced by the engine per revolution, is

$$L = L_1 + L_2.$$

The combination of the two formulas then gives also

$$L_1 = \frac{\lambda(1+m)}{\lambda-1}L \quad \text{and} \quad L_2 = -\frac{1+m\lambda}{\lambda-1}L. \quad (130)$$

Therefore if only one of the three quantities of work is known, the other two can at once be determined.

In hot-air engines the work  $L$  is positive, i.e., work is produced; consequently the work  $L_1$  is produced by the piston in the hot space, while the piston in the cold space consumes work.

As regards the heat quantity  $dQ$  which, for example, is to be imparted to the hot space, we can find it from equation (47a), p. 203, in case this space is the discharging space, otherwise it is found from equation (48a), p. 204. As we may assume that the air from the regenerator enters with the temperature which exists in the receiving space, i.e., may insert  $T_x = T_y$  in the last equation, then the term  $c_p(T_y - T_x)dG_y$  disappears and the two equations (47a) and (48a) become identical; the difference between receiving and discharging space disappears therefore as soon as the regenerator is on hand.

The heat quantity  $Q_1$  which is to be supplied to the heating space accordingly follows from the integration of the equation

$$-AV_x dp = -Ad(V_x p) + ApdV_x,$$

and the heat quantity  $Q_2$  for the cold space by the integration of

$$-AV_y dp = -Ad(V_y p) + ApdV_y.$$

For a complete turn the initial and final values of the products  $V_x p$  and  $V_y p$  are the same, consequently the two heat quantities per turn are

$$Q_1 = AL_1 = \frac{\lambda(1+m)}{\lambda-1}AL \quad (131)$$

and

$$Q_2 = AL_2 = -\frac{1+m\lambda}{\lambda-1}AL. \quad (132)$$



Therefore both these quantities can be directly determined from the indicator diagrams of the two cylinders, always provided that the regenerator is on hand.

We recognize that the preceding propositions completely agree with those already found on p. 359; a very important result which will be discussed more fully later.

Only one question is still to be settled, namely, the determination of at least one of the three quantities of work  $L$ ,  $L_1$ , or  $L_2$ .

For this purpose we must first determine the law according to which the pressure  $p$  varies with the crank angle  $\omega$ ; if we utilize equations (126) and (127) in equation (129) there will follow

$$\frac{2\lambda BGT_2}{p} = (1+m\lambda)V_1(1-\cos \omega) + \lambda(1+m)V_2(1+\cos(\omega+\delta)).$$

Or if, for the purpose of simplification, we substitute

$$\frac{1+m\lambda}{\lambda(1+m)} \frac{V_1}{V_2} = a, \quad \dots \quad (133)$$

we can also write

$$\frac{2BGT_2}{p(1+m)V_2(1+a)} = 1 - \left( \frac{a-\cos \delta}{a+1} \cos \omega + \frac{\sin \delta}{a+1} \sin \omega \right)$$

Furthermore if we introduce the abbreviations  $c$ ,  $r$ , and  $\alpha$ , according to the following scheme:

$$\left. \begin{aligned} \frac{2BGT_2}{(1+m)V_2(1+a)} &= c, \\ \frac{a-\cos \delta}{a+1} &= r \cos \alpha, \\ \frac{\sin \delta}{a+1} &= r \sin \alpha, \end{aligned} \right\} \dots \quad (134)$$

we shall finally get

$$p = \frac{c}{1-r \cos(\omega-\alpha)}; \quad \dots \quad (135)$$

as this formula is the polar equation of an ellipse, referred to the focus, the pressure  $p$  can very readily be found graphically, for

different crank angles  $\omega$ , and when introduced into the piston-force diagram, Fig. 55, the curve *DDD* presents to the eye its law of change.

The matter becomes very simple when there is given the greatest and least pressure in the course of the cycle, namely,  $p_1$  and  $p_2$ ; we have the first value from equation (135) for  $\omega = \alpha$  and the other for  $\omega = 180^\circ + \alpha$ ; therefore

$$p_1 = \frac{c}{1-r} \quad \text{and} \quad p_2 = \frac{c}{1+r},$$

and from the combination of these equations follows

$$r = \frac{p_1 - p_2}{p_1 + p_2} \quad \text{and} \quad c = \frac{2p_1 p_2}{p_1 + p_2}, \quad . \quad . \quad . \quad . \quad (136)$$

while the combination of the second and third of equations (134) gives, for the auxiliary angle  $\alpha$ ,

$$\tan \alpha = \frac{\sin \delta}{a - \cos \delta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (137)$$

We can now proceed to the determination of one of the three work quantities  $L_1$ ,  $L_2$ , or  $L$ ; let us determine the work  $L_1$  per turn for the hot cylinder (Fig. 55). The pressure  $p$  varies with the crank angle  $\omega$  in the first semicircle, according to equation (135); in the second semicircle, however, if we estimate  $\omega$  anew from the second dead-point, the pressure  $p$  is found from the formula

$$p = \frac{c}{1+r \cos (\omega - \alpha)}.$$

If we differentiate equation (126) we get for the work  $L'$  (work of expansion) in the first semicircle

$$L' = -\frac{V_1 c}{2} \int_0^\pi \frac{d(\cos \omega)}{1 - r \cos (\omega - \alpha)},$$

and the work  $L''$ , the work of compression, in the second semi-circle

$$L'' = + \frac{V_1 c}{2} \int_0^\pi \frac{d(\cos \omega)}{1 + r \cos (\omega - \alpha)}.$$

If we perform the indicated integrations, we can find, after some circumlocution, the work  $L_1$  per revolution for the hot space, because  $L_1 = L' - L''$ :

$$L_1 = \pi \frac{V_1 c}{r} \left[ \frac{1}{\sqrt{1 - r^2}} - 1 \right] \sin \alpha,$$

or, if we utilize the relations (136),

$$L_1 = \pi \sqrt{p_1 p_2} \frac{\sqrt{p_1} - \sqrt{p_2}}{\sqrt{p_1} + \sqrt{p_2}} V_1 \sin \alpha.$$

If we utilize the third of equations (134), also equation (133) and the first of equations (130), we get the work  $L$  of the engine per turn:

$$L = \pi \frac{(\lambda - 1) V_1 V_2 p_2}{(1 + m \lambda) V_1 + \lambda (1 + m) V_2} \frac{\phi (\phi^2 + 1)}{(\phi + 1)^2} \sin \delta, \quad (138)$$

where

$$\phi = \sqrt{\frac{p_1}{p_2}} \dots \dots \dots (139)$$

It is worthy of note that the calculation for the mean value of the ordinate of the curve  $DDD$  of the piston diagram in Fig. 55 leads to the simple expression  $\sqrt{p_1 p_2}$ .

With the foregoing everything has been given that is necessary for judging a Rider engine with a regenerator. For if the engine work  $L$  is known from equation (138), we can also determine both the heat quantities  $Q_1$  and  $Q_2$  from equations (131) and (132).

Besides we see from equation (138) that, other things being equal, the work  $L$  is greater, the greater we choose the angle of advance  $\delta$ ; consequently it will be best to place the crank of the

cold cylinder  $\delta=90^\circ$  ahead of the crank of the hot cylinder. If the crank is made to follow, which would be the case for example in Fig. 55 if the engine ran in the opposite direction, the  $\sin \delta$  and consequently  $L$  will become negative.

**Example.** If we substitute in the present case, as in example on p. 362,

$$\lambda=2, \quad \frac{p_1}{p_2}=2.5, \quad m=0.495; \quad V_1=V_2, \quad \text{and} \quad \delta=90^\circ,$$

there follows, according to equation (138),

$$L=0.5239 V_2 p_2,$$

or if we assume the lower pressure  $p_2$  equal one atmosphere,  $p_2=10333$  kg. [2116.3 lb.], we get

$$L=5413 V_2 [L=1108.7 V_2].$$

If we take both pistons of the same diameter  $d=250$  mm. [10 in.] and of the same stroke  $s_1=s_2=300$  mm. [12 in.], the volume of the cylinder becomes

$$V_2=0.014726 \text{ cbm. } [V_2=0.52006 \text{ cu. ft.}],$$

and therefore the work per revolution

$$L=79.71 \text{ mkg. } [576.55 \text{ ft.-lb.}],$$

or for  $u=140$  revolutions per minute

$$N=2.48 \text{ horse power } [2.446].$$

According to equations (131) and (132) the heat quantities per revolution amount to

$$Q_1=0.5621 \text{ cal. and } Q_2=-0.3741 \text{ cal.} \\ [Q_1=2.2306 \text{ B.t.u. and } Q_2=-1.4845 \text{ B.t.u.}]$$

The quantity of heat which is to be supplied hourly to the hot cylinder amounts to 1904 cal. [8030 B.t.u.], and the heat quantity which must be withdrawn from the cold cylinder in the same time is 1267 cal. [5344 B.t.u.]. If the cooling water is heated through  $10^\circ \text{ C.}$  [ $18^\circ \text{ F.}$ ], then the cooling water per hour per horse power is 51.09 kg. [121.14 lb.]. The ratio  $L_1$  to  $L_2$  of the work of the two cylinders can be computed for the present example from the equation (130):

$$\frac{L_1}{L_2} = \frac{\lambda(1+m)}{1+m\lambda} = 1.50,$$

and the heat quantities  $Q_1$  and  $Q_2$  bear the same ratio to each other.

Unfortunately there are no experiments which permit a comparison with the results of calculation, at least they give no clue to the real air

volume  $V_0$  of the regenerator and concerning the temperature ratio  $\lambda$ . Some experiments by Schöttler<sup>1</sup> on a Rider engine gave for the ratio  $L_1:L_2$  values lying between 2.16 and 2.40, according to which the value of  $\lambda$  for this experimental engine must be taken considerably greater than 2. Schöttler's experiments show the ratio brake power to indicated power to be remarkably unfavorable; the ratio, on the average, turns out to be 0.42 and therefore about one-half of what it is in steam engines. It will be left for future experiments to decide what corrections must be applied to the above-developed formulas, which were derived without considering the clearance space and under the assumption of complete action of the regenerator, in order to bring about an agreement between calculated and experimental results.

The way in which the indicator diagrams I and II of the hot and cold cylinders, respectively, are drawn from the pressure curve  $DD$  (the piston-force diagram) in Fig. 55, p. 367, is directly evident from the figure; but both diagrams may be shown in combination by a third diagram (III), which I call the resultant indicator diagram of the Rider engine; we get it when we lay off from a point  $O$  (Fig. 55, III) the value  $V_z = V_0 + V_x + V_y$  as abscissa, and lay off  $p$  as its ordinate. Utilizing equations (126) and (127), p. 367, we get

$$V_z = V_0 + \frac{V_1 + V_2}{2} - \frac{1}{2}[(V_1 - V_2 \cos \delta) \cos \omega + V_2 \sin \delta \sin \omega], \quad (140)$$

where  $V_z$  is the total volume of the air in the engine at the instant represented by the pressure  $p$ .

If we substitute

$$\left. \begin{aligned} V_1 - V_2 \cos \delta &= V \cos \delta_0, \\ V_2 \sin \delta &= V \sin \delta_0, \end{aligned} \right\} \quad . . . . . (141)$$

where  $V$  and  $\delta_0$  are two constant quantities whose meaning will immediately be evident, we get

$$V = \sqrt{V_1^2 + V_2^2 - 2V_1V_2 \cos \delta} \quad . . . . . (142)$$

and

$$\tan \delta_0 = \frac{V_2 \sin \delta}{V_1 - V_2 \cos \delta}, \quad . . . . . (143)$$

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<sup>1</sup> Compare reference on p. 345.

and consequently from equation (140)

$$V_z = V_0 + \frac{V_1 + V_2}{2} - \frac{1}{2} V \cos^* (\delta_0 - \omega) \quad . \quad . \quad (140a)$$

The formula leads to a minimum and a maximum for  $V_z$  when  $\omega = \delta_0$  and  $\omega = \delta_0 - \pi$  respectively; the difference of these two eminent values is  $V$ ; consequently this value, determined by equation (42), represents the piston displacement when the whole cycle, represented by diagram III (Fig. 55), takes place in one cylinder.

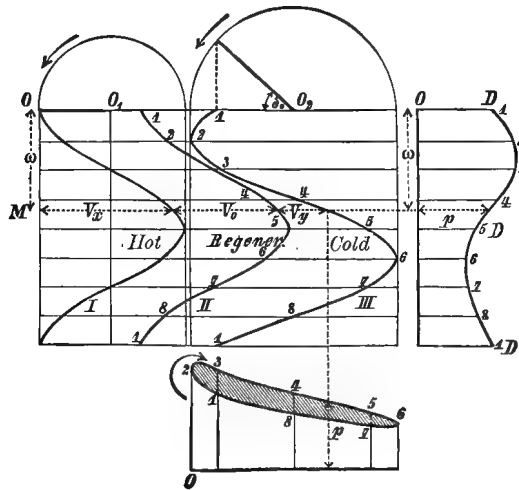


FIG. 56.

This remark at once suggests that exactly the same cycle, developed in the preceding for the Rider engine, can also be described with the Lehmann arrangement, and that exactly the same formulas will hold as soon as the Lehmann engine is provided with a regenerator and the following notation is used.

If we lay off on the vertical through  $O$  (Fig. 56) the crank angle  $\omega$  as abscissa  $OM$ , and lay off from  $M$ , to the right, the ordinates  $V_x$ ,  $V_x + V_0$  and  $V_x + V_0 + V_y$ , where  $V_x$  and  $V_y$  are to be computed from equations (126) and (127), p. 367, then we shall

get three curves; the first two curves I and II give the travel of the transfer-piston (piston diagram) per revolution, and curve III gives the travel diagram for the power-piston (see Fig. 54, p. 362). If the pressure curve  $DD$  is likewise drawn as a function of  $\omega$ , we find, as is at once evident from the indications of Fig. 56, the several points of the indicator diagram, which is identical with diagram III of Fig. 55, and which in the *Lehmann* engine is directly obtained by means of an indicator.

If  $V_1$ ,  $V_2$ , and  $\delta$  are given for the *Rider* engine, then  $V$  and  $\delta_0$  are readily found from equations (142) and (143) for the *Lehmann* engine, which is to describe the same cycle.

For example if  $V_1 = V_2$  and  $\delta = 90^\circ$ , then in the *Lehmann* engine the piston displacement  $V$  of the power engine must be  $V = V_1\sqrt{2}$  and the crank of this piston must follow the crank of the transfer-piston at the angle  $\delta_0 = 45^\circ$ .

On the other hand if, in the *Lehmann* engine (with a regenerator),  $V_1$ ,  $V$ , and  $\delta_0$  are given, then  $V_2$  and  $\delta$  are calculated by equations (141); we find

$$V_2 = \sqrt{V_1^2 + V^2 - VV_1 \cos \delta_0},$$

$$\tan \delta = \frac{V \sin \delta_0}{V_1 - V \cos \delta_0},$$

and thus, to a certain extent, we have reduced the *Lehmann* engine to the *Rider*; its work can now be determined by equation (138) and the remaining quantities can be found from the formulas there developed.

## § 64. ERICSSON'S CLOSED HOT-AIR ENGINE.

As a winding up of the preceding investigations we will devote a short consideration to one more engine, which *Ericsson* proposed as early as 1833, but which is little known; much later, about 1850, the name of this clever man became generally known among engineers, by his inventing two other hot-air engines which, however, are open air engines. If we here return to this older idea of *Ericsson's* it is because the engine in question can be regarded, from the theoretical point of view, as the

fundamental form of all caloric (heat) engines, taking this designation in its broadest sense.<sup>1</sup>

In a tubular boiler *AA* (Fig. 57) there is air of the pressure  $p_1$ ; the boiler is surrounded by a vessel *B* in which there is a fluid of high temperature, continuously delivering heat to the air in the boiler; the liquid may be called the heating fluid, and may under certain circumstances consist of fire gases, i.e., may consist of the products of combustion of high temperature which come from a furnace. While the boiler *AA* represents the heating apparatus, a second tubular boiler *EE* constitutes a cooling apparatus; the air flowing through the latter is cooled by a cooling body (water), which plays around the tubes (flowing in at *m* and flowing out at *n*).

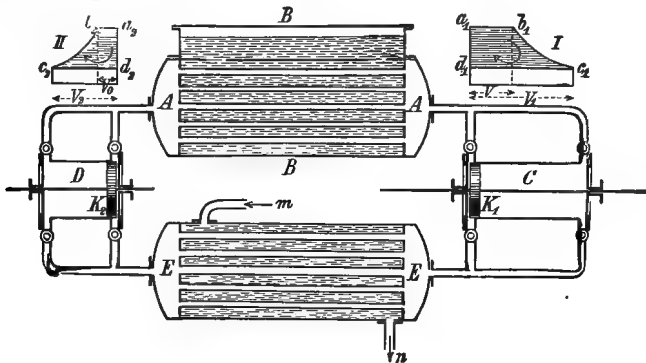


FIG. 57.

The two cylinders *C* and *D*, in which the pistons  $K_1$  and  $K_2$  move, are connected with apparatus *A* and *E* in a way evident from Fig. 57; the connections are air channels, which are provided with valve gear (cocks, valves, or slides). In the heating apparatus the pressure is  $p_1$ , the pressure prevailing in the cooling apparatus is  $p_2$ ; the capacity of the two spaces, relatively to the cylinder contents, is, however, to be so great that the pressure in the apparatus, during an engine period, can be regarded as nearly invariable.

The piston  $K_1$ , in the cylinder *C*, stands at the left end, and now, while the piston sweeps through the space  $a_1b_1 = V$ , the

<sup>1</sup> "Zur Theorie der Kaltdampfmaschinen," Civilingenieur, Vol. 27, 1881, p. 449.



$G$  kg. [lb.] weight of air leaves the boiler  $A$  and enters the cylinder with the pressure  $p_1$  and the temperature  $T_1$ . At the end of the piston travel  $V$  let the connection with the boiler cease, and let the air now expand, according to the pressure curve  $b_1c_1$ , from the volume  $V$  to the volume  $V_1$ ; the pressure sinks from  $p_1$  to  $p_2$ , and the temperature  $T_1$  to  $T_3$ . Now connect the space to the left of the piston  $K_1$  with the interior of the cooling apparatus  $EE$ , and push the air out of the space  $V_1$ , along the path  $c_1d_1$ , under constant pressure  $p_2$ , through the cooling apparatus to the second cylinder  $D$ , where the air moves the piston  $K_2$  along the path  $d_2c_2$ , through the space  $V_2$ , under constant pressure  $p_2$ ; during the passage through the cooling apparatus, the temperature of the air is brought down from  $T_3$  to  $T_2$ ; now, shutting off the air cylinder  $D$  from the cooling apparatus  $E$ , the air is compressed along the path  $c_2b_2$  till the pressure has risen from  $p_2$  to  $p_1$ , and then the air is pushed back, under constant pressure, into the heating apparatus  $AA$ ; during compression the volume diminishes from  $V_2$  to  $V_0$  and the temperature increases from  $T_2$  to  $T$ .

The hatched areas of the two indicator diagrams are herewith traversed in the direction of the given arrows. The diagram to the right gives the work  $L_1$  which is performed per stroke in the cylinder  $C$ , the power or expansion cylinder, and the area of the diagram to the left gives the work  $L_2$  consumed in the cylinder  $D$ , the feed or compression cylinder.

The work (indicated)  $L$  of the engine, per stroke, then follows from the difference  $L_1 - L_2$ .

As the air weight  $G$ , per stroke, leaves the compression cylinder  $D$  and enters the heating apparatus with the temperature  $T$ , leaving the latter with a temperature  $T_1$  when it passes over to the expansion cylinder  $C$ , the quantity of heat  $Q_1$  entering the heating apparatus is

$$Q_1 = c_p G (T_1 - T). \quad . \quad . \quad . \quad . \quad . \quad . \quad (144)$$

During the return of the piston, the same quantity of air is pushed into the cooling apparatus at temperature  $T_3$  and leaves this compartment at a temperature  $T_2$ ; consequently the heat quantity

$Q_2$  which is withdrawn per stroke from the air by the cooling body is

$$Q_2 = c_p G (T_3 - T_2). \quad (145)$$

Theoretically considered, expansion according to the curve  $b_1c_1$  and compression  $c_2b_2$  take place adiabatically; if we substitute  $n$  for  $\kappa$ ,  $n < \kappa$ , thus assuming a polytropic change of state so as to partly take account of the influence of the cylinder walls, and assume this value of  $n$  to be known, we have the relation

$$\frac{T_1}{T_3} = \frac{T}{T_2} = \left( \frac{p_1}{p_2} \right)^{\frac{n-1}{n}}; \quad (146)$$

furthermore, if we use the data of Fig. 57 for the volume successively occupied by the air weight  $G$  at these principal points of the cycle, we get

$$BG = \frac{Vp_1}{T_1} = \frac{V_1p_2}{T_3} = \frac{V_2p_2}{T_2} = \frac{V_0p_1}{T}. \quad (147)$$

The work  $L_1$  produced in the expansion cylinder  $C$  is composed of the work  $Vp_1$  at the entrance, the work  $V_1p_2$  at the exit and the work of expansion measured according to equation (7b), p. 154, is

$$\frac{1}{n-1} (Vp_1 - V_1p_2),$$

from which follows

$$L_1 = \frac{n}{n-1} (Vp_1 - V_1p_2),$$

or, with the utilization of the relations (147),

$$L_1 = \frac{n}{n-1} BG (T_1 - T_3). \quad (148)$$

In like manner is found the work  $L_2$  which is expended in the compression cylinder  $D$ :

$$L_2 = \frac{n}{n-1} BG (T - T_2). \quad (149)$$

and, accordingly, the work  $L$  of the engine per double stroke is

$$L = c_p \frac{n(\kappa-1)}{\kappa(n-1)} \frac{G}{AT} (T_1 - T)(T - T_2) \quad . \quad . \quad . \quad (150)$$

when we eliminate  $T_3$  by equation (146) and replace the constant  $B$  according to equation (54), p. 134.

If the engine is double-acting and makes  $u$  revolutions per minute, then the indicated work  $N$  in horse powers is given by

$$N = \frac{Lu}{30 \times 75} \left[ N = \frac{Lu}{30 \times 550} \right] \quad . \quad . \quad . \quad . \quad (151)$$

and therewith the theory of the engine is finished.

For an engine which is to be designed there can be regarded as given, the work  $N$  and the number of revolutions  $u$ , the upper and lower temperature limits, namely, the temperature  $T_1$  at which the air leaves the heating apparatus, and the temperature  $T_2$  at which the air leaves the cooling apparatus; besides this there are known the limiting pressures  $p_1$  and  $p_2$  and the exponent  $n$ .

Then the intermediate temperatures  $T$  and  $T_3$  can be determined from equations (146), and the air weight  $G$  per stroke, which flows through the engine, is found from a combination of equations (150) and (151); with this the basis is won for finding the heat quantities  $Q_1$  and  $Q_2$  according to equations (144) and (145), and for finding from equation (147) the volumes  $V_1$ ,  $V_2$ ,  $V$ , and  $V_0$ ; the dimensions of the cylinder can be derived from the last magnitudes.

The engine describes exactly the cycle which has already been described in § 51, p. 292, and was especially discussed there with reference to Fig. 41. The engine does not possess a regenerator and therefore describes an imperfect cycle; but it would be easy, as was at one time suggested by Ericsson, to improve the cycle by the insertion of a regenerator. The regenerator ought to be arranged so that the air will flow through it during the passage from the expansion cylinder  $C$  to the cooling apparatus  $E$ , and so that the air will traverse it in the opposite direction when passing from the cooling cylinder  $D$  to the heating apparatus  $A$ .

If we follow the earlier presentation, it would not be difficult to examine the action of the regenerator under the assumptions made; nor would it be difficult to extend the theory of the engine before us by considering the clearance spaces and by assuming incomplete expansion; we will omit doing this because the engine proposed by Ericsson fifty years ago has not come into use.

One advantage this engine possesses over those fully discussed above: it renders possible the use of greater heating surfaces; it is probably owing to the want of these that the Lehmann, Rider, and Lauberau-Schwartzkopff engines, with and without regenerator, have not been generally introduced.<sup>1</sup>

A common objection to all hot-air engines is that their dimensions are much too large in comparison with their performance, and in this respect the steam engines are far preferable. But this comparison is not a perfectly just one because, in making it, the space occupied by the heating and boiler plant of the steam engine is left out of account.

An attentive examination of the proposition developed in the whole preceding section may perhaps strengthen the view that possibly the hot-air engines might replace the steam engines for small powers, because, when provided with the regenerator, their cycle is not at all behind that of the steam engine in efficiency; in fact it excels because it can be worked between wider temperature limits. The greater cylinder dimensions can be endured

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<sup>1</sup> Napier and Rankine were the first to clearly recognize the great importance of increasing the heating and cooling surfaces as much as possible; their patented hot-air engine (*Mechanic's Magazine*, 1854, No. 1628; *Dingler's Polytechnisches Journal*, Vol. 135, 1855, p. 241) must be regarded as essentially an improved Stirling engine; like the latter it is double-acting and provided with a regenerator; the power cylinder is separated from the transfer-piston cylinder as in the Lauberau-Schwartzkopff engine, only in the latter the regenerator is left out and the engine is made single-acting, changes which may be characterized as backward steps. The Napier and Rankine engine did not come into use; but perhaps, by reversing it and transforming it into a closed cold-air engine, its principal part may be utilized, namely, its transfer-piston, which is provided with a regenerator that possesses at each end a series of cylindrical metallic rods which crowd out the air by entering piston fashion into pipes closed at the outer end.

and may be reduced by designing high-speed engines and, when possible, by choosing the lower limit of pressure  $p_2$  considerably greater than the atmospheric pressure, that is, by employing high pressure; all the formulas developed for the performance, which were found for the engines treated in the foregoing articles, show that the indicated work is directly proportional to the pressure  $p_2$ , other things being equal.

Of course here the circumstance that the air losses increase as the pressure rises acts as a handicap.

The remarkably few brake and indicator experiments<sup>1</sup> do not yet suffice for the formation of a final judgment; to be sure the results of these experiments offer little encouragement for the introduction and further consideration of hot-air engines.

### (b) Open Hot-air Engines.

#### § 65. ENGINES WITH AND WITHOUT REGENERATOR.

During each period the open engine draws in a new cylinder volume of external atmospheric air and pushes it out again at the end of the cycle.

Fig. 58 gives the schematic representation of such an engine without regenerator and appears to have come directly from Fig. 57, p. 377, by leaving out the cooling apparatus  $EE$  there drawn. The admission pipes  $m_1$  and  $m_2$  of the compression cylinder  $D$ , and the exhaust pipes  $n_1$  and  $n_2$  (Fig. 58) of the expansion cylinder  $C$ , open directly into the free atmosphere.

When the piston moves from right to left it sucks in, through the pipe  $m_2$ , the external atmospheric air of the pressure  $p_2$  and of the temperature  $T_2$ ; during the return stroke of the piston the air is compressed, according to the pressure curve  $c_2b_2$  of the indicator diagram II, from the volume  $V_2$  to the volume  $V_0$  and its pressure is raised from  $p_2$  to  $p_1$ , and, with the temperature  $T$  thus acquired, is then forced under constant pressure  $p_1$  into the heating apparatus. Here it is heated from  $T$  to  $T_1$  and it then

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<sup>1</sup> Experiments of Slaby, Schöttler (compare references on p. 353).

enters with the pressure  $p_1$  the expansion cylinder  $C$ , where its volume increases from  $V_0 = a_2 b_2$  to  $V = a_1 b_1$ . In the cylinder  $C$  it now expands, according to the curve  $b_1 c_1$  of indicator diagram I, to the atmospheric pressure  $p_2$  and is now pushed along the path  $c_1 d_1$ , through the exhaust-pipe  $n_1$ , into the open air under the constant pressure  $p_2$ , and the temperature  $T_3$ , which it reaches by expanding to the point  $c_1$ . The engine is assumed to be double-acting; during the return of the piston the air enters through the pipe  $m_1$  and leaves by the pipe  $n_2$ .

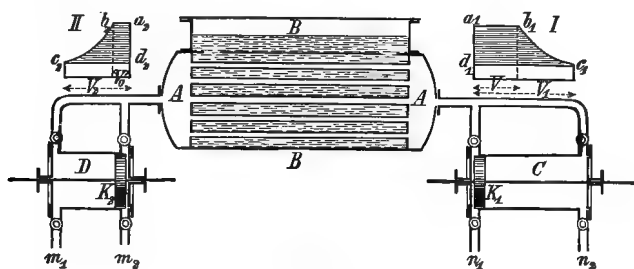


FIG. 58.

The theory is again completely given by formulas (144) to (151), p. 378, with, of course, the same limitations there imposed; the whole difference consists in this, that in the open engine the lower pressure  $p_2$  is the atmospheric pressure, while in the closed engine it may be larger or smaller than this. The temperature limits  $T_1$  and  $T_2$  are chosen in the open engine as in the closed one. The engine may be provided with a regenerator, as was suggested by Ericsson; the air coming from the expansion cylinder  $C$  must then be led through the regenerator into the open air, and during the reverse motion the compression cylinder  $D$  must suck in fresh atmospheric air through the regenerator.

The more generally known Ericsson engine, as well as the engine arrangements of Johnson<sup>1</sup> and Wilcox,<sup>2</sup> are to be classed with the here discussed system of open engines.

<sup>1</sup> Dingle's Polytechnisches Journal, 1869, Vol. 178, p. 417.

<sup>2</sup> Ibid., 1863, Vol. 170, p. 312.

## B. COLD-AIR ENGINES.

### (a) Closed Cold-air Engines.

#### § 66. REVERSAL OF THE ERICSSON CLOSED HOT-AIR ENGINE.

Every hot-air engine, whatever its arrangement may be, can be transformed, by reversing the cycle, into a cold-air engine, a cold-producing (refrigerating) machine. Here also we can distinguish between closed and open engines; at the present time it is the latter kind which are more widely used.

Machines for producing cold and manufacturing ice undoubtedly have a great future; although it is to be expected that hereafter there will be generally used machines which employ vapors (of ammonia, carbonic acid, etc.) in place of atmospheric air; these machines I have called cold-vapor engines, and I will return to them later. Nevertheless it seems appropriate to here discuss more fully the cold-air engines, because they have been extensively used for the cooling of spaces, particularly those employed for meat preservation.

Cold-air engines of the closed type are not in use; so far as I know there is only one construction proposed, and that one by Kirk.

Kirk utilized the reversal of a Stirling engine with a regenerator, whose arrangement may be inferred from the scheme shown in Fig. 52, p. 341, where the transfer-piston  $K_1$  is provided on the inside with a regenerator; such an engine is said to have produced 212 pounds (avoirdupois) of ice in 24 hours with one horse power, which corresponds to 4 kg. ( $8\frac{1}{2}$  lb.) per hour per horse power, a performance which is certainly very small, for in the more recent Linde ammonia-vapor engine the production is estimated at 25 kg. of ice (55 lb.) per hour per (brake) horse power.

For the fuller investigation of a closed air engine we will discuss the reverse of the hot-air engine sketched in Fig. 57, p. 377. In Fig. 59 the sketch is repeated, but the two indicator diagrams I and II are replaced by diagrams III and IV of Fig. 59a, p. 386, in which is entered the temperature notation which will be employed in the following calculations.

Suppose the tubular boiler  $AA$  to contain air of a pressure  $p_1$  and of a temperature  $t_1$  which is below  $0^\circ \text{C}$ . ( $32^\circ \text{F}$ .); the boiler is surrounded by a casing  $B$  in which there is a solution of cooking salt or chloride of calcium which does not freeze even when it also is cooled below  $0^\circ \text{C}$ . ( $32^\circ \text{F}$ .).

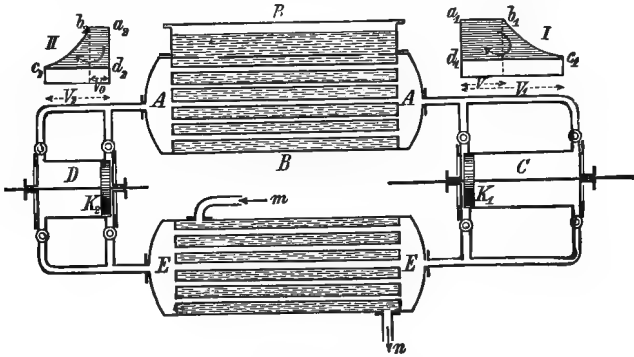


FIG. 59.

The salt solution is regarded as a heating fluid, because its temperature is somewhat higher than that in the boiler  $AA$ .

The continuous operation of the machine keeps the temperature of the air in the heating apparatus  $AA$  at a low value, so that heat is continuously withdrawn from the salt solution; therefore if tin cans containing fresh water are dipped into the brine the water in the cans will be frozen, or the cool brine can be conducted by pipes to places where cooling is to be effected and the warm brine is then led back to the casing  $B$  for renewed cooling.

For the presentation of the cycle of the machine, suppose piston  $K_1$  in cylinder  $C$  to pass from left to right, and suppose the space to the left of  $K_1$  to be in communication with the boiler space  $AA$ ; if the boiler space is large enough the piston  $K_1$  will suck in air under the constant pressure  $p_1$ ; let the temperature



with which the air leaves the boiler be  $T_1$ ; at the end of the piston stroke shut-off takes place and the air in the cylinder  $C$  is compressed according to pressure curve  $c_1b_1$  (diagram III, Fig. 59a); in so doing the volume diminishes from  $V_1$  to  $V$ , the pressure rises from  $p_1$  to  $p_2$ , and the temperature likewise grows from  $T_1$  to  $T_3$ .

Now let the air along the path  $b_1a_1$  be pushed, under constant pressure  $p_2$ , through the cooling apparatus  $EE$  to the second cylinder  $D$ , where it pushes back piston  $K_2$ , under constant pressure  $p_2$ ,

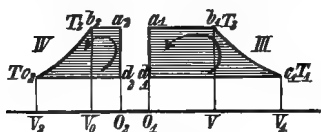


FIG. 59a.

along the path  $a_2b_2=V_0$  (diagram IV, Fig. 59a); in its passage through the cooling apparatus it is cooled by cold water, which flows about the tubes of the cooling apparatus, entering at  $m$  and

leaving at  $n$  (Fig. 59); here the air is cooled from  $T_3$  to  $T_2$  and expands in the cylinder  $D$ , after being cut off from the cooling vessel, according to the curve  $b_2c_2$  (diagram IV) till the pressure has again fallen to the value  $p_1$  in the heating apparatus, in order that it may finally be pushed back along the path  $c_2d_2$ , into the space  $AA$ , under the constant pressure  $p_1$ . During expansion the temperature sinks from  $T_2$  to  $T$ , and the volume grows from  $V_0$  to  $V_2$ .

Let us assume that during each piston stroke  $G$  kg. [lb.] of air are withdrawn from the heating apparatus at one end by cylinder  $C$  and are supplied to it at the other end by cylinder  $D$ , then the heat quantity  $Q_1$  which is furnished by the brine to the air in vessel  $A$  is

$$Q_1 = c_p G (T_1 - T). \quad (1)$$

On the other hand the heat quantity  $Q_2$  which is withdrawn, per stroke, in the cooling apparatus from the air is

$$Q_2 = c_p G (T_3 - T_2). \quad (2)$$

Furthermore if we assume the two curves  $b_1c_1$  and  $b_2c_2$  to be adiabatic lines, then between the pressures and temperatures there

will exist the known relation

$$\frac{T_3}{T_1} = \frac{T_2}{T} = \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}}, \dots \dots \dots (3)$$

and we get the volume of the air at the several, main, points of the cycle (Fig. 59a) from the equations

$$BG = \frac{V_1 p_1}{T_1} = \frac{V p_2}{T_3} = \frac{V_0 p_2}{T_2} = \frac{V_2 p_1}{T}. \dots \dots \dots (4)$$

The work  $L_1$ , consumed per revolution in cylinder  $C$ , which here acts as compression cylinder, is found in the same way as that taken when deriving equations (148) and (149), p. 379; it is

$$L_1 = \frac{\kappa}{\kappa-1} BG(T_3 - T_1). \dots \dots \dots (5)$$

On the other hand the work  $L_2$  produced per revolution in cylinder  $D$ , which is here the expansion cylinder, is

$$L_2 = \frac{\kappa}{\kappa-1} BG(T_2 - T). \dots \dots \dots (6)$$

The difference of these two quantities of work gives the driving work  $L$  of the engine per double stroke, i.e., the indicated work taken theoretically, provided we use relation 54, p. 134,

$$AL = c_p G[(T_3 - T_1) - (T_2 - T)],$$

or, eliminating  $T_3$ , with the help of equation (3),

$$L = \frac{c_p G}{AT}(T_2 - T)(T_1 - T). \dots \dots \dots (7)$$

This equation is identical with equation (150), p. 380, if we there assume adiabatic expansion and compression in the hot-air engine, i.e., assume  $n = \kappa$ , only the work quantity  $L$  appears with the opposite sign, as it ought, for in the hot-air engine the work  $L$  is produced, while in the cold-air engine it is consumed as driving work.

If we divide equation (7) by equation (1) we get the simple relation

$$\frac{AL}{Q_1} = \frac{T_2 - T}{T}. \quad . . . . . (8)$$

As the cooling water has the atmospheric temperature, the temperature  $T_2$  need only be taken a little greater; the preceding equation therefore teaches that with a particular value of  $Q_1$  the work  $L$  will be larger the lower we go with the temperature  $T$ ; as this value represents the lowest temperature occurring in the cycle, the rule ought to be followed not to place the lower limit of temperature any further down than is absolutely necessary for the cooling process contemplated.

In the designing of refrigerating machines we regard as given the heat quantity which must be continuously withdrawn from the brine in a unit of time. If we assume the second as the unit, and designate the heat quantity in question by  $Q_s$ , then if we substitute  $Q_s$  for  $Q_1$ , equation (8) will give the theoretical (indicated) driving work  $L_s$  per second,

$$L_s = \frac{Q_s}{AT}(T_2 - T), \quad . . . . . (9)$$

or, if we express the work in  $N$  horse powers, and assume the engine as double-acting and making  $u$  revolutions per minute, we get

$$N = \frac{Q_s}{75 AT}(T_2 - T). \quad . . . . . (10)$$

$$[N = \frac{Q_s}{550 AT}(T_2 - T)].$$

If we determine  $G$  from the first of equations (4), namely, from

$$ABG = \frac{AV_1 p_1}{T_1},$$

and substitute it in equation (7) we get

$$L = \frac{\kappa}{\kappa - 1} \frac{(T_2 - T)(T_1 - T)}{TT_1} V_1 p_1,$$

and therefore follows, because

$$L = 30 \times 75 \frac{N}{u} \quad \cdot$$

$$\left[ L = 30 \times 550 \frac{N}{u} \right],$$

for the computation of the volume  $V_1$  of the compression cylinder  $C$ , the formula

$$V_1 p_1 = \frac{\kappa - 1}{\kappa} \times 30 \times 75 \frac{T T_1}{(T_2 - T)(T_1 - T)} \frac{N}{u} \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

$$\left[ V_1 p_1 = \frac{\kappa - 1}{\kappa} \times 30 \times 550 \frac{T T_1}{(T_2 - T)(T_1 - T)} \frac{N}{u} \right].$$

From equations (4) we then get volume  $V_2$  of the expansion cylinder

$$V_2 = \frac{T}{T_1} V_1. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

The ratio of compression in cylinder  $C$  and the ratio of expansion in cylinder  $D$  follow from the same equations:

$$\frac{V}{V_1} = \frac{V_0}{V_2} = \frac{p_1 T_2}{p_2 T} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

**Numerical Example.** In a closed cold-air engine of the presented sort the brine in casing  $B$  (Fig. 59, p. 385) is to be permanently kept at  $-10^\circ$  to  $-15^\circ$  C. [ $+14^\circ$  to  $+5^\circ$  F.] for the purpose of ice production.

We assume that the air is sucked in by the compression cylinder at the temperature  $T_1 = 258^\circ$  ( $-15^\circ$  C.) [ $+5^\circ$  F.] from the heating apparatus  $A$ , further that the air leaves the cooling apparatus at the temperature  $T_2 = 293^\circ$  ( $+20^\circ$  C.) [ $+68^\circ$  F.] to enter the expansion cylinder; let the pressure in the latter  $p_2 = 3p_1$ , hence three times  $p_1$  in the heating apparatus; then from equation (3) we get

$$\frac{T_3}{T_1} = \frac{T_2}{T} = 1.3764.$$

From this follows the temperature at the end of the compression in the compression cylinder  $T_3 = 355.1^\circ$  ( $+82.1^\circ$  C.) [ $179.78^\circ$  F.], and the temperature at the end of the expansion in the expansion cylinder is  $T = 212.9^\circ$  ( $-60.1^\circ$  C.) [ $-76.18^\circ$  F.].

From equation (10) we have

$$N = 2.1279 Q_s [N = 0.52866 Q_s],$$

and from equation (11)

$$V_1 p_1 = 9944 \frac{N}{u} \\ \left[ V_1 p_1 = 72923 \frac{N}{u} \right].$$

In order to produce ice of  $0^\circ \text{ C.}$  [ $32^\circ \text{ F.}$ ] from 1 kg. [lb.] of water at  $0^\circ \text{ C.}$  [ $32^\circ \text{ F.}$ ], it is necessary to withdraw from the water 79 calories [142.2 B.t.u.] of heat; if the water has a temperature of  $t^\circ \text{ C.}$  [ $t^\circ \text{ F.}$ ] and if there is to be produced from it ice at  $-t_0^\circ \text{ C.}$  [ $t_0^\circ \text{ F.}$ ], then there must be withdrawn from the water the heat quantity  $79 + t + ct_0$  [ $142.8 + t + ct_0$ ], where  $c$  is the specific heat of the ice, which amounts to  $c = 0.5$ . If on the average we assume  $t = 15^\circ$  [ $59^\circ \text{ F.}$ ] and  $t_0 = -8^\circ$  [ $17.6^\circ \text{ F.}$ ] in order that the ice may become as solid as possible, we get, in round numbers, 100 calories [180 B.t.u.]; we can therefore assume that in practice we must withdraw 100 calories [180 B.t.u.] of heat from one kilogram [pound] of water at ordinary atmospheric pressure, in order to make good ice out of it.

Now if the present machine is to deliver hourly 250 kg. [550 lb.] of ice, there must be withdrawn from the brine every hour 25000 calories [99208 B.t.u.] of heat, therefore  $Q_s = \frac{25000}{3600} = 6.9444 \text{ cal.}$  [ $Q_s = 27.558 \text{ B.t.u.}$ ], and according to the last equation but one

$$N = 14.78 \text{ horse powers, [14.569].}$$

Taking into account the resistances neglected in the preceding calculation, we ought to add 25% for the determination of the real work of driving; if this refrigerating machine is driven by a steam engine, the latter must develop an effective work of about 18.5 horse powers.

If the assumed machine makes  $u = 50$  revolutions per minute, and if the lower limit of the pressure is one atmosphere so that  $p_1 = 10,333 \text{ kg.}$  [2116.3 lb.], then the second of the preceding formulas gives for the cubic capacity of the compression cylinder

$$V_1 = 0.2844 \text{ cbm. [10.040 cu. ft.],}$$

while the capacity of the expansion cylinder, according to equation (12), is

$$V_2 = 0.2347 \text{ cbm. [8.285 cu. ft.];}$$

in the actual construction the two values ought to be taken somewhat larger. By dividing equations (2) and (1), p. 386, there follows

$$\frac{Q_2}{Q_1} = \frac{T_3 - T_2}{T_1 - T} = 1.377.$$

If we refer  $Q_2$  to the second, and hence substitute the value given above, we get for the heat quantity which must be withdrawn from the air per second, in the cooling apparatus,

$$Q_2 = 9.562 \text{ cal. [37.947 B.t.u.].}$$

If the cooling water, in its passage through the cooling apparatus, is heated through  $5^\circ \text{ C. [} 9^\circ \text{ F.]}$  there will be necessary per second 1.912 kg. [4.2 lb.] and hourly 6883 kg. [15120 lb.] of cooling water.

A closed cold-air engine (refrigerating machine) of the kind just discussed has neither been built nor proposed;<sup>1</sup> the results of the numerical example do not seem to be unfavorable so far as the necessary dimensions of the two cylinders are concerned; of course as regards the size of the heating surface in the heater  $AA$ , and of the cooling surface in the cooler  $EE$  (Fig. 59, p. 385), some special observations ought first to be made. In one particular, however, there is a prominent defect, the driving work turns out to be considerable; for example, a cold-vapor engine (Linde's system) working with ammonia vapor, which we will discuss later, will require only half the driving work for the same output as the just calculated air machine. The difference is due to the fact that in air machines of the assumed kind the lower temperature limit must be taken very low in order not to get extraordinary engine dimensions; the results of computation are more favorable when we have in view not ice production, but the circulation of the brine, for in the latter case the cooling need not be carried so far.

For future comparison with cold-vapor engines, the following is of consequence.

If we completely leave out the expansion cylinder  $D$  (Fig. 59, p. 385) and let the air flow from the cooling apparatus, where it is under higher pressure anyway, and allow it to flow directly through a connecting pipe, provided with a regulating valve, back into the heating apparatus, the air will enter the latter at the temperature  $T$ , corresponding to the lower limit, will enter with the

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<sup>1</sup> In this connection we have also neglected to discuss theoretically the cold-air engine of the proposed Ericsson system provided with a counter-current apparatus, as ought to have been done in accordance with Lorenz's data. In the cold-vapor engine account will be taken of this newer view.

same temperature with which it is introduced by the expansion cylinder of our machine. Nevertheless a great difference will still exist. If we assume, as is permissible, that the flow takes place from the cooler, under the constant pressure  $p_2$ , into the heating apparatus, against the constant counter-pressure  $p_1$ , and if we designate by  $w$  the velocity with which the air enters the heating apparatus, then theoretically (equation 33a, p. 247), neglecting the resistances, the relation

$$AG\frac{w^2}{2g} = c_p G(T_2 - T) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

will hold.

Comparison with equation (6), p. 387, which can be brought to the same form, gives

$$AG\frac{w^2}{2g} = AL_2,$$

according to which the indicator area IV (Fig. 59a, p. 386) also expresses the work in the form of kinetic energy which is found in the  $G$  kg. [lb.] of air entering per stroke. But the air, under the constant pressure  $p_1$ , spreads itself into the heating apparatus from the entrance orifice, and passes into a condition of rest, in doing which the kinetic energy is transformed into heat.

If  $T'$  is the temperature of the air after the spreading, then the relation

$$AG\frac{w^2}{2g} = c_p G(T' - T)$$

obtains, and comparison with formula (14) shows the result  $T' = T_2$ .

If we wish to bring back the air directly into the heating apparatus, without the interposition of the feed or expansion cylinder  $D$ , then the machine will be entirely ineffectual because a temperature  $T'$  will nearly establish itself there, which is identical with the temperature  $T_2$  which the air has assumed in the cooling apparatus. The expansion cylinder constitutes a necessary and essential part of the cold-air engine (refrigerating machine) of the assumed sort. In this respect the circumstances are very different in the closed, cold-vapor engines (which will be shown

later to possess exactly this arrangement), where, in fact, the expansion cylinder is omitted without essential detriment to the cycle.

Closer reflection, moreover, shows that in the closed cold-air engines the use of a regenerator is as much to be recommended as in the hot-air engines; it has already been mentioned that Kirk proposed to transform the Stirling engine, by reversal, into a closed cold-air engine (refrigerating machine); but it seems to me that the Rider engine is, constructively, better suited for such a reversal, for with it, probably, the heating and cooling surface can be most easily increased in the manner pursued by Napier and Rankine in their hot-air engine.

### § 67. REVERSAL OF THE RIDER CLOSED HOT-AIR ENGINE.

Fig. 60 repeats the schematic representation of a Rider engine (Fig. 55, p. 367). Now suppose the jacket  $D$  of cylinder  $B$

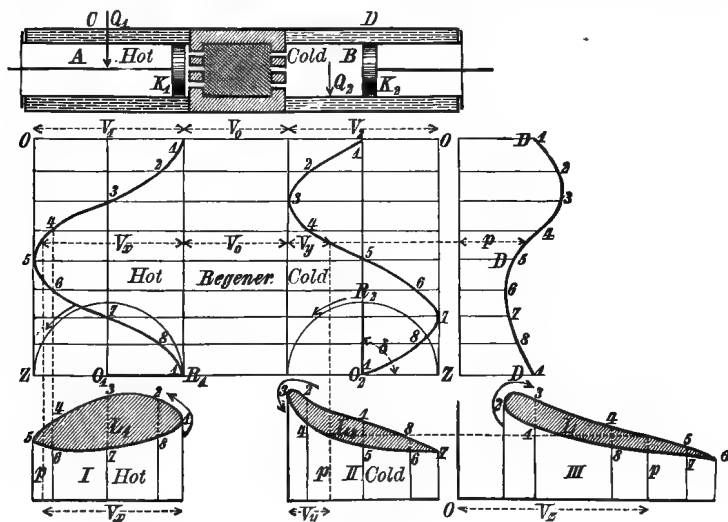


FIG. 60.

to be washed out by a cold brine, and suppose the jacket  $C$  of cylinder  $A$  to be traversed by the cooling water, then we have only



to conceive all the arrows of the figure to be reversed; the air in the cylinder  $B$ , at the lower temperature limit  $T_2$ , absorbs per period or revolution (the engine is single-acting) the heat quantity  $Q_2$  and gives off in the cylinder  $A$ , to the cooling water, the heat quantity  $Q_1$  at the higher temperature  $T_1$ . The indicator diagram I of cylinder  $A$  now represents consumed work, and diagram II of cylinder  $B$ , work produced; the difference of the two quantities of work is represented by the resultant diagram III and is the theoretical (indicated) driving work  $L$  of the cold-air engine now before us. Moreover the engine runs in the same direction as it did when we assumed that we were dealing with a hot-air engine; the crank of piston  $K_2$  here also is ahead of the crank of piston  $K_1$  by the angular distance  $\delta$  (in the figure  $\delta = 90^\circ$  is assumed).

Here, too, are valid all the formulas developed from p. 367 to p. 373, with the sole difference that the heat quantities  $Q_1$  and  $Q_2$  and the work quantities  $L_1$ ,  $L_2$ , and  $L$  occur with opposite signs; we can therefore simply refer to this part, so far as the notation of the formula and the theory of the engine is concerned.

The driving work per revolution is, according to equation (138), p. 372,

$$L = \pi \frac{(\lambda - 1)V_1V_2p_2}{(1 + m\lambda)V_1 + \lambda(1 + m)V_2} \frac{\phi(\phi^2 + 1)}{(\phi + 1)^2} \sin \delta; \quad \dots \quad (15)$$

the heat quantity  $Q_2$ , withdrawn from the brine per revolution, is, according to equation (132), p. 369,

$$Q_2 = \frac{1 + m\lambda}{\lambda - 1} AL, \quad \dots \quad (16)$$

and the quantity of heat which is to be absorbed in the same time, from the cooling water, follows from equation (131), p. 369:

$$Q_1 = \frac{\lambda(1 + m)}{\lambda - 1} AL. \quad \dots \quad (17)$$

If in equation (16) the heat quantity  $Q_2$  is referred to the second

and designated by  $Q_s$ , we get the driving work of the machine in horse powers:

$$N = \frac{\lambda - 1}{1 + m\lambda} \frac{Q_s}{75 A} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$\left[ N = \frac{\lambda - 1}{1 + m\lambda} \frac{Q_s}{550 A} \right],$$

while in equation (15), when the engine makes  $u$  revolutions per minute, we must substitute

$$L = 60 \times 75 \frac{N}{u} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$\left[ L = 60 \times 550 \frac{N}{u} \right]$$

**Numerical Example.** If we assume the ratio  $\lambda$  of the two temperatures  $T_1$  and  $T_2$  to be  $\lambda = 1.25$ , which gives for a temperature  $T_2 = 238^\circ$  ( $-35^\circ$  C.) [ $-31^\circ$  F.] in cylinder  $B$ , to a temperature  $T_1 = 297.5$  ( $+24.5^\circ$  C.) [ $-76.1^\circ$  F.] in cylinder  $A$  (Fig. 60), and if we estimate the value  $m$ , discussed on p. 368 and belonging to the regenerator, to be  $m = 0.5$ , then the preceding equation (18) gives the driving work:

$$N = 0.870 Q_s$$

$$[N = 0.216 Q_s].$$

If we choose the angle of advance  $\delta = 90^\circ$ , make the two cylinders equally large, i.e., take  $V_1 = V_2$ , and assume that the greatest pressure  $p_1$  occurring in the cycle bears to the least,  $p_2$ , the relation  $p_1 = 2.5 p_2$ , then combination with equations (15) and (19) gives

$$V_2 p_2 = 24143 \frac{N}{u}$$

$$\left[ V_2 p_2 = 177050 \frac{N}{u} \right],$$

because here (p. 372)

$$\phi = \sqrt{\frac{p_1}{p_2}} = 1.5811.$$

If the machine is to withdraw hourly from the brine 25000 calories [99208 B.t.u.] of heat, then, according to the preceding formula, the theoretical driving work for  $N$  is

$$N = 6.04 \text{ horse powers } [5.953].$$

If the lower value of the pressure is one atmosphere, then  $p_2 = 10333$  kg. [2116.3 lb.], and if the engine makes  $u = 50$  revolutions per minute, then

according to the last of the preceding formulas the cubic capacity of the two cylinders must be

$$V_1 = V_2 = 0.2822 \text{ cbm. [9.961 cu. ft.].}$$

If we divide equation (17) by equation (16) we get

$$\frac{Q_1}{Q_2} = \frac{\lambda(1+m)}{1+m\lambda} = 1.154.$$

If we refer the heat quantities to the second, then, for the present case, the heat quantity which the cooling water must withdraw from the heat per second is 8.0140 cal. [31.8 B.t.u.] or 28850 cal. [114500 B. t.u.] per hour.

The driving work of this engine seems considerably smaller than that found for the machine of the preceding example on p. 389; this is due to the use of the regenerator and to the circumstance that the lower temperature limit is not taken so low; of course the cylinder dimensions are much larger, but the engine is single-acting and there is no special heating or cooling apparatus.

Although some uncertainty still attaches to the assumptions underlying the calculations, which can only be removed by experiments on, and experience with, actually constructed engines, nevertheless it does seem possible that the construction of closed cold-air engines (refrigerating machines) of the kind described, will be attended with success. Engineers ought therefore to attack the problem; the cold-producing engines, of course in the form of cold-vapor engines, have been extensively used and not simply for purely technical purposes, but have also been proposed for the cooling of dwellings in hot countries. The cooling of air in dwellings, by a system of pipes in which the cold fluid circulates, is accompanied by a condensation on the pipes of the moisture of the atmospheric air, and experience shows, and Linde first called attention to it, that this condensation contains an appreciable amount of absorbed carbonic acid. Therefore the cooling of the air is accompanied by a purification of the air which ought to be of great importance hygienically for home life in tropical countries.

## (b) Open Cold-air Engine.

## § 68. REVERSAL OF THE ERICSSON CLOSED HOT-AIR ENGINE WITH THE HEATING APPARATUS LEFT OUT.

In the schematic representation of the closed hot-air engine (Fig. 57, p. 377) suppose the heating apparatus  $AA$  and its jacket to be left out, and reverse the cycle there discussed, then we get the open cold-air engine as it is often built and as it is schematically represented in the following figure (61).

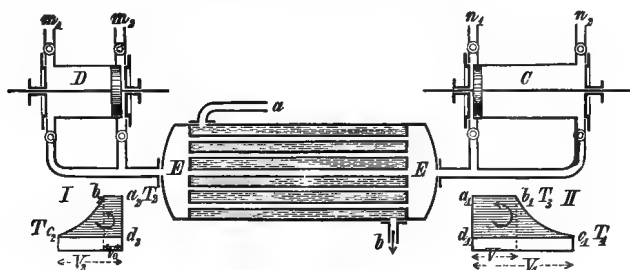


FIG. 61.

$C$  is again the compression cylinder which, through the pipes  $n_1n_2$ , alternately sucks in the external atmospheric air, compresses it, and forces it through the cooling apparatus  $EE$  to the expansion cylinder  $D$ ; there the cooled air expands from the upper pressure limit  $p_2$ , again to the atmospheric pressure  $p_1$ , and is pushed out of the cylinder under the constant pressure  $p_1$  through the pipes  $m_1m_2$ ; the two pipes  $m_1m_2$  unite in forming a conduit through which the cooled air is conducted to the space in which cooling is to be effected. The cooling of the air, which has been heated in the machine by compression, is effected in the cooling apparatus  $EE$  by cold water, which is supplied at  $a$  and discharged through the pipe  $b$ . Of the two indicator diagrams I and II the former belongs to the expansion cylinder and the latter to the compression cylinder.

The theory of this engine is contained simply and completely in the formulas which have been developed for the closed engine on pp. 386 to 390.

The whole difference is that the values of the pressure  $p_1$  and the temperature  $T_1$  in the open engine correspond to those of the outer atmosphere; it therefore seems unnecessary to further explain this engine cycle by numerical calculations.

In the practical constructions, however, in spite of the great simplicity of these engines a peculiar obstacle is encountered, which is the reason why this machine, well known in principle, was introduced so late and with such difficulty.<sup>1</sup> As the external atmospheric air always contains more or less vapor, or water, snow is formed in the expansion cylinder, and because new quantities of air are continuously driven through the machine it is formed in such quantities that in a short time the air channels are stopped up with snow; further, when high pressure is used, i.e., great compression in the compression cylinder, the marked rise in temperature connected with it acts injuriously upon the packing. The removal of the latter evil has been attempted by injecting cold water into the compression cylinder, but this increased the moisture of the air in the expansion cylinder and increased the formation of snow. Although the stoppage of the conduits could be removed by special designing, say by inserting special snow chambers, nothing would be gained by it, for the performance of the machine is extraordinarily reduced by the snow formation itself.

On board ships and in great slaughter-houses the open air engines of Bell-Coleman have been employed for the cooling of meat. In these engines water is injected into the compression cylinder and from this the air leaves the cooling space, where cooling-off results from more water jets (not from surface cooling); from this space the air enters the upper part of a tower-like vessel and deposits the water part of its mixture; from here the air passes through a pipe, which is led through the space that is to be cooled by the machine, and then goes to the expansion cylinder. The whole arrangement is based on the correct idea of supplying the expansion cylinder with air, already cooled as much as possible, for the moisture capacity of air is smaller, the lower its temperature. The whole manipulation occurs at the expense

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<sup>1</sup> The first open cold-air engine was built by an American, G o r r i e.

of the engine performance, and it is therefore very questionable whether the suppression of snow precipitation is not too dearly bought, particularly as it is not even completely removed in this way. In the cold-vapor engines all these difficulties disappear; unfortunately there is still a complete lack of experimental results for comparison. Of course the experiments should not be confined simply to the cooling action of the two engine types, but should help to decide the question as to the amount of driving work needed by the two kinds of engines for an equal production of cold. One can hardly doubt that the comparison will be unfavorable to the open cold-air engine; but the circumstances are doubtless different in the closed cold-air engines, for in them the loss of air by leakage can be covered by the introduction of new air and this can be artificially dried beforehand. Kirk suggested, for this purpose, a vessel filled with a solution of chloride of calcium.

## II. Theory of Internal-combustion Engines.

### § 69. PRELIMINARY REMARKS.

By an internal-combustion engine is always understood one in which the process of combustion, with the accompanying heat development and the production of a gas mixture capable of doing work, takes place in the interior of the engine. In the air engine considered above (as in steam engines) the fuel and the air necessary for its combustion were separated from the mediating body in the working cylinder; consequently the real working cycle was distinguished from the combustion process in the heating plant and was treated separately in the theoretical elucidations, as was particularly emphasized in § 53, p. 300.

In the internal-combustion engines the fuel, the air necessary for combustion, and the products of combustion constitute the working body which here takes the place of the mediating body

of the air engine considered above and, like it, serves to produce work by suitable changes of pressure and volume.

Here the important difference exists that in the course of the working cycle *chemical* changes of the working body occur; these were hitherto specially excluded in all the developments of the present treatise, and particularly so in the derivation of the general laws of thermodynamics of the first section. Therefore, as far as is possible at the present time, account will be taken of the influence of the chemical occurrences in the internal-combustion engines.

The view has always been held, although not always definitely expressed, that the process of converting heat into work would be more perfect in the internal-combustion engines; from this thought, in the course of time, there has sprung a whole series of proposals for experimental constructions of such engines, in which solid, liquid, and gaseous fuels and explosives should, and did, find application. The success of all these efforts of recent times must be characterized as perfectly extraordinary, although a whole series of questions still remains, which can only be answered experimentally.

Among engines which at the present time seem to be most perfectly designed, we must emphasize the "gas engine" or "gas motor" in the form presented by Otto.

In these engines *illuminating gas* mixed with atmospheric air and a part of the gaseous products of combustion left behind from the preceding period, are ignited in the working cylinder, after being subjected to a preliminary compression.

At the present time engines are extensively used which work with the so-called *producer gas* which is generated by passing air and steam through the glowing layers of coal in a furnace. The name Dowson-gas comes from the name of the Englishman Dowson who invented the process; the working part of this gas consists principally of carbonic oxide gas, while in the engine run with illuminating gas different hydrocarbons constitute the explosive constituent.

The motors run with illuminating gas can of course only be driven in connection with a gas plant, while the motors run by

producer gas generate their own gas supply; consequently these motors are in general only available for comparatively small powers.

Very considerable powers are developed by engines which utilize blast-furnace gas, and in recent times their details have been greatly perfected; these gases likewise mainly contain carbonic oxide.

In all the engines mentioned at the end of the explosive-like combustion the cylinder contains the gaseous products of combustion in a condition of high pressure and high temperature, which are then allowed to expand so far that at the end of the piston stroke the pressure has come down nearly to atmospheric pressure; then, during the return of the piston in the working cylinder, a part of the cylinder contents are retained and the rest are thrust into the open air. The engine is therefore an open one, for during each period a new charge of illuminating gas and atmospheric air must be taken in.

In addition to gas engines, motors have been extensively used and have led to ingenious constructions in which liquid fuels were employed, for instance benzine, petroleum and alcohol.

For the production of the fuel mixture of the charge for the working cylinder, the atmospheric air is driven through liquid benzine and thus saturated with benzine vapors; in petroleum engines, on the other hand, the petroleum is sprayed, evaporated by contact with hot walls, and then mixed with air. The further procedure, ignition and work, resembles the occurrences in the gas engine.

It is not in keeping with the plan of the present book to go more fully into the construction and peculiarities of the aforesaid engine types; for the thermodynamic side of the question it completely suffices to discuss the principal representative of this type, the Otto gas engine, and take up first, theoretically, the process of combustion of a mixture of illuminating gas and air.

As an appendix the starting points and successes of the newest efforts of the Diesel Motor will be discussed.



## A. OTTO'S GAS ENGINE.

### § 70. PISTON MOTION IN THE FOUR-CYCLE ENGINE.

In Fig. 62 are shown the cylinder and the piston diagram of an Otto engine;  $K_1$  and  $K_2$  give the piston position at the two ends of the stroke; to the left of the extreme piston position

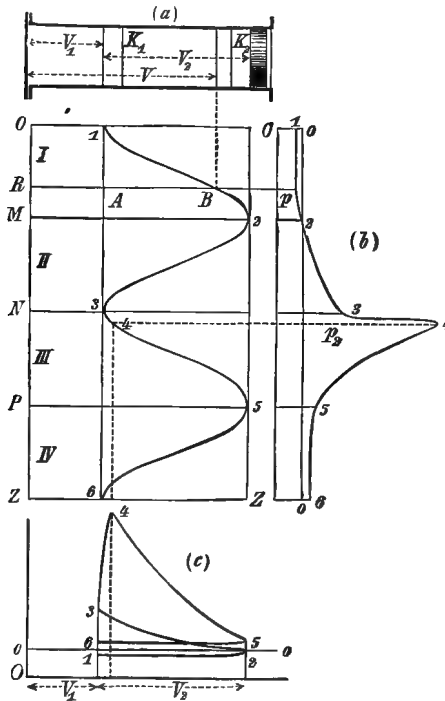


FIG. 62.

$K_1$  there is a dead space which may be called the compression space, and its volume be designated by  $V_1$ . In the piston diagram the vertical distance  $OZ$  represents the time for two revolutions of the crank, or, if uniform rotation is assumed, it represents the path then traversed by the crank-pin. The whole cycle, taking the figure as a basis, takes place to the left of the piston; to the right of it, because here the cylinder is open, the atmospheric pressure prevails, whose action is here left out of account, because the work expend-

ed in overcoming it, during the forward motion, is regularly produced on the return motion.

At the beginning of the period the piston stands at 1, and the compression space is filled with gaseous products of combustion of approximately atmospheric pressure, but of comparatively high temperature, i.e., with gases which have been left over

in the cylinder from the preceding period. The vertical stretch  $OZ$  is here divided into four parts; in the first portion  $OM$  of the time, or during the first half revolution of the crank, the piston goes from left to right; at the time  $OR=t$ , the piston has traveled the distance  $AB$  and the volume of the gas in the cylinder at this instant is measured by the distance  $RB$ ; in the second portion  $MN$  of the time the piston goes back, and in the third and fourth portions of time the piston motion repeats itself. The working cycle is therefore distributed over four portions of time, and hence the engine has been called half-acting, or is said to be of the four-cycle type. Fig. 62*b* represents the corresponding piston-force diagram, the ordinate  $Oo$  represents the atmospheric pressure, hence the vertical line  $oo$  represents the so-called atmosphere and  $OZ$  the line of zero pressures.

In the first stage (I) the piston sucks in atmospheric air and illuminating gas, and thus, to a certain degree, there occurs a mixture with the products of combustion initially present in the space  $V_1$ ; the pressure in the cylinder is represented by the ordinates of the curve portion 1-2 of Fig. 62*b*; the pressure is here, and nearly to the end of the piston stroke, smaller than the atmospheric pressure.

At point 2, shut-off takes place, and then during the return stroke of the piston the gas quantity is compressed to the volume  $V_1$  and in so doing the pressure rises in accordance with curve 2-3.

At the point 3 (i.e., at the dead-point) ignition now takes place, the pressure increases rapidly, almost suddenly, according to curve 3-4 (Fig. 62*b*); as in so doing the piston is already upon the return path, this portion of the curve, in reality, rises in a somewhat sloping fashion; during the rest of the third phase (III) expansion takes place, and shortly before the end of the piston stroke the exhaust port opens so that the last portion 4-5 of the curve represents expansion with exhaust; finally in the fourth phase the quantity of gas developed by the combustion and corresponding to the piston displacement  $V_2$  is pushed into the open air; the pressure, which is represented by the portion 5-6 of the curve, is nearly constant and somewhat greater than the atmospheric pressure.

The real indicator diagram in Fig. 62c was derived from the piston-force diagram, Fig. 62b; but as regards the connection between these two diagrams what is necessary has been said during the discussion of hot-air engines; besides, it is so simple that no further explanations are here required.

The indicator diagram in Fig. 62c (the sketch corresponds in general to the practically observed diagram) is enclosed in a loop-like curve; the upper part of the area corresponds to positive, produced work, the lower part, on the other hand, to negative; the latter area nearly disappears in the actually obtained diagrams, for here the curved portions 5-6 and 1-2 nearly coincide with the atmospheric line *o-o*.

It is worth remarking that according to what has preceded Otto's engine is a compression pump in the first and second phases, it sucks in gas and air and compresses the mixture; it is only in the third and fourth phases that it is really a driving engine and conducts the real working process. The two processes can be separated; the suction and compression can be undertaken in a special cylinder, a compression pump, and during the compression the gas mixtures can be forced into the second cylinder (the power-cylinder), in which explosion, expansion, and discharge into the open air occur. This arrangement underlies the Körtling gas engine; here two indicator diagrams appear which, superimposed, likewise produce the diagram represented in Fig. 62c.

The examination of physical occurrences, however, now demands the study of the real process of combustion in the power-cylinder and of the experimental data on hand concerning it.

## § 71. THE BEHAVIOR OF COMBUSTIBLE GASES DURING IGNITION.

In order to embrace all cases which arise, let us suppose a combustible gas to consist of  $n_1$  atoms of carbon (C),  $n_2$  atoms of hydrogen (H),  $n_3$  atoms of oxygen (O), and  $n_4$  atoms of nitrogen (N), then the chemical notation for this gas is

$$(C_{n_1}H_{n_2}O_{n_3}N_{n_4}). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we designate in their order the atomic weights of the several elements C, H, O, and N by  $e_1$ ,  $e_2$ ,  $e_3$ , and  $e_4$ , then the molecular weight  $m$  of the contemplated gas is

$$m = n_1e_1 + n_2e_2 + n_3e_3 + n_4e_4 = \Sigma(ne); \quad . \quad . \quad . \quad . \quad (2)$$

here we may substitute (see p. 105)

$$e_1 = 12, \quad e_2 = 1, \quad e_3 = 16, \quad e_4 = 14.$$

The constant  $B$  of the equation of condition of this gas, namely, of the equation  $pv = BT$ , can be found from relation (14), p. 105:

$$Bm = B_0m_0,$$

where the factors in the right member refer to hydrogen; now since  $m_0 = 2$  and because we can use with sufficient accuracy  $B_0 = 424$  for all the following investigations (see p. 106), we can determine  $B$  from the equation

$$ABm = 2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and then, for a given pressure  $p$  and given temperature  $T$ , immediately find the specific volume  $v$  of this gas from the equation of condition.

Now let this gas be mixed with another gas which consists of a mixture of oxygen and nitrogen in the proportion of  $\alpha$  kg. [lb.] of oxygen and  $\beta$  kg. [lb.] of nitrogen in the unit of weight; let  $q$  kg. [lb.] of this gas be employed with one kg. [lb.] of the given gas, which can be designated as combustible gas.

If we assume  $m$  kg. [lb.] of the last-mentioned gas, then the total mixture consists of  $m$  kg. [lb.] combustible gas,  $q m \alpha$  kg. [lb.] of oxygen, and  $q m \beta$  kg. [lb.] of nitrogen.

The constant  $B$  of the equation of condition for the combustible gas follows from equation (3), the constants for oxygen and nitrogen are to be taken from the table on p. 104; hence the constant  $B_m$ , which corresponds to the total mixture, is found from equation (19a), p. 108:

$$B_m = \frac{\frac{2}{Am} + (26.472\alpha + 30.131\beta)q}{q+1} \dots \dots \dots (4)$$

$$\left[ B_m = \frac{\frac{2}{Am} + (48.251\alpha + 54.920\beta)q}{q+1} \right].$$

Moreover, if for the combustible gas the specific heat at constant pressure is  $c_p$ , and  $c_v$  that for constant volume, and if  $c_p'$  and  $c_v'$  designate similar values for the whole mixture, we get from equations (13a) and (14a), p. 173,

$$c_p' = \frac{c_p + (0.2175\alpha + 0.2438\beta)q}{q+1} \dots \dots \dots (5)$$

and

$$c_v' = \frac{c_v + (0.1551\alpha + 0.1727\beta)q}{q+1}, \dots \dots \dots (6)$$

by utilizing the values given on pp. 119 and 125. If the mixture supplied to the combustible gas is ordinary atmospheric air, then we may substitute in the preceding formulas, according to p. 126,  $\alpha=0.2356$  and  $\beta=0.7644$ ; on the other hand if pure oxygen instead of air is added we must substitute  $\alpha=1$  and  $\beta=0$ .

This gas mixture is now to be ignited; if the combustion is a perfect one the carbon burns to carbonic acid, the hydrogen burns to water, and the result is a new gas mixture consisting of carbonic acid, steam, oxygen, and nitrogen, provided the temperature after combustion is so high that the resulting water is present as vapor. Since one atom of carbon takes up two atoms of

oxygen when changing to carbonic acid ( $\text{CO}_2$ ), i.e., when  $e_1$  kg. [lb.] carbon requires  $2e_3$  kg. [lb.] oxygen, then on the whole the  $n_1$  atoms of carbon in the gas considered require  $2n_1e_3$  kg. [lb.] of oxygen, and the weight  $G_1$  of carbonic acid, resulting from combustion, amounts to

$$G_1 = n_1(e_1 + 2e_3) \text{ kg. [lb.]} \quad . \quad . \quad . \quad . \quad (7a)$$

On the other hand when water ( $\text{H}_2\text{O}$ ) is formed there will be a half atom of oxygen for every atom of hydrogen, or for  $e_2$  kg. [lb.] there will be needed  $0.5e_3$  of oxygen; as the contemplated gas possesses  $n_2$  atoms its combustion will require  $0.5n_2e_3$  kg. [lb.] of oxygen; hence the weight  $G_2$  of the resulting water amounts to

$$G_2 = n_2(e_2 + 0.5e_3) \text{ kg. [lb.]} \quad . \quad . \quad . \quad . \quad (7b)$$

Further if, in the contemplated gas, there are present, according to equation (2),  $n_3e_3$  kg. [lb.] of oxygen, the added mixture contains  $qm\alpha$  kg. [lb.] of oxygen. The weight  $G_3$  of the oxygen left over is therefore

$$G_3 = n_3e_3 + qm\alpha - 2n_1e_3 - 0.5n_2e_3 \text{ kg. [lb.]} \quad . \quad . \quad (7c)$$

Finally the weight  $G_4$  of the nitrogen, at the end of combustion, is

$$G_4 = (n_4e_4 + qm\beta) \text{ kg. [lb.]} \quad . \quad . \quad . \quad . \quad (7d)$$

because the nitrogen effects no changes. The addition of the four preceding weights, when we consider equation (2), again leads, as it ought, to the value  $m(q+1)$ , i.e., to the weight of the whole mixture before combustion.

Now taking in order the four gases, carbonic acid, steam, oxygen, and nitrogen, we have for the corresponding constants  $B$  of the equation of condition:

19.204,	46.954,	26.472,	and	30.131
[35.003,	85.583,	48.251,	and	54.920],

furthermore the specific heats at constant pressure ( $c_p$ ) are

0.2169,	0.4805,	0.2175,	and	0.2438,
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and the specific heats at constant volume ( $c_v$ )

$$0.1718, \quad 0.3695, \quad 0.1551, \quad \text{and} \quad 0.1727;$$

then we can calculate for the mixture resulting from the combustion from the formulas given on pp. 108 and 172:

$$B = \frac{\Sigma(GB)}{\Sigma(G)}, \quad c_p = \frac{\Sigma(Gc_p)}{\Sigma(G)}, \quad c_v = \frac{\Sigma(Gc_v)}{\Sigma(G)}. \quad . \quad . \quad (8)$$

while the similar values before ignition were calculated above and designated by  $B_m$ ,  $c_p'$ , and  $c_v'$ .

If the pressure, specific volume, and temperature before ignition are  $p'$ ,  $v'$ , and  $T'$ , and after it  $p$ ,  $v$ , and  $T$ , then the relations

$$pv = BT \quad \text{and} \quad p'v' = B_m T',$$

hold.

If we suppose the pressure and temperature after combustion to be brought back to the values which they possessed before ignition, then the last two expressions give

$$\frac{v}{v'} = \frac{B}{B_m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and from this we can conclude whether a change of volume is connected with combustion.

To be sure the given calculations lay no claim to great accuracy because just for carbonic acid and for steam the above-given specific heats are uncertain, particularly for carbonic acid, for which these magnitudes vary with the temperature; neither are the two vapors subject to the equation of condition for gases, and here it is especially the vapor of water for which it is only permissible at low pressures and high temperatures to assume that it follows the law of *Mariotte and Gay-Lussac*.

The combustible gases have usually atmospheric temperature before ignition; then if we lead the gas mixture, after combustion, back to the initial temperature, the water will no longer be present in the form of vapor but will appear almost completely

condensed; as the water volume is almost infinitesimal in comparison with the other gases it would have been more correct in determining  $B$  from equation (8) to have substituted  $G_2=0$ , for the weight of the steam present after combustion, in place of the weight given by equation (7b).

Equation (7c) gives rise to a special remark bearing on the weight of oxygen left over after combustion and enables us to calculate it. If we substitute  $G_3=0$  we get here, from the relation

$$q\alpha = (2n_1 + 0.5n_2 - n_3)e_3, \quad . \quad . \quad . \quad (10)$$

the minimum weight  $q$  of the mixture composed of oxygen and nitrogen which must be supplied for the combustion of 1 kg. [lb.] of gas in order to effect perfect combustion. If this mixture consists of atmospheric air, we must substitute, as was mentioned above,  $\alpha=0.2356$ , while we must assume  $\alpha=1$  when pure oxygen is used.

Let us assume as a special case that the principal constituent, namely marsh gas (light hydrocarbon), is to be burned with a supply of atmospheric air. For this gas we have the chemical formula  $\text{CH}_4$ ; therefore, according to equation (1),  $n_1=1$ ,  $n_2=4$ ,  $n_3=0$ ,  $n_4=0$ , and hence, according to equation (2), the molecular weight is

$$m = 1 \times 12 + 4 \times 1 = 16,$$

and according to equation (3) the constant  $B$  of the equation of condition is

$$B = 53.000 \quad [B = 96.604].$$

From equation (10) then follows, because  $e_3=16$ ,

$$q\alpha = 4.$$

For complete combustion, therefore, at least 4 kg. [lb.] of pure oxygen must be supplied for 1 kg. [lb.] of marsh gas; the minimum of the atmospheric air necessary is, on the other hand (because  $\alpha=0.2356$ ),

$$q = 16.978 \text{ kg. [lb.]}$$

Let us now assume that in reality 1 kg. [lb.] of this gas is, before ignition, mixed with  $q=24$  kg. [lb.] of atmospheric air;



as we must assume for marsh gas  $c_p=0.5929$  and  $c_v=0.4680$ , there is found from equations (4), (5), and (6), p. 406, for the total mixture before ignition,

$$B_m=30.218 \quad [B_m=55.079], \quad c_p'=0.2518, \quad c_v'=0.1872, \quad \frac{c_p'}{c_v'}=1.345.$$

If we have  $m=16$  kg. [lb.] of marsh gas before ignition, the total weight of the mixture will be

$$m(q+1)=400 \text{ kg. [lb.]}$$

If we substitute the given values in equations (7a) to (7d) we get, after combustion:  $G_1=44$  kg. [lb.] of carbonic acid;  $G_2=36$  kg. [lb.] of water,  $G_3=26.47$  kg. [lb.] of oxygen, and  $G_4=293.53$  kg. [lb.] of nitrogen. From equations (8) therefore follows, for the whole mixture resulting from the combustion,

$$B=30.201 \quad [B=55.048], \quad c_p=0.2604, \quad c_v=0.1891, \quad \frac{c_p}{c_v}=1.377.$$

The values differ but little from those which belong to the mixture before combustion. In this comparison the water present is regarded as a vapor; now if in consequence of subsequent cooling of the products of combustion it had become liquid, we should get  $B=25.975$  [47.345]; in the first case, for the same pressure and the same temperature, the volumes before and after combustion,  $v'$  and  $v$ , will, according to equation (9), be almost exactly equal; in the second case there will be a contraction and we shall have  $v=0.859 v'$ .

## § 72. BEHAVIOR OF COAL (ILLUMINATING) GAS DURING IGNITION.

Illuminating gas is composed of a series of separate gases, and indeed the proportions of the mixture are very variable; for the purpose of general investigation it will be best to assume a certain mixture of average proportions; in order to facilitate comparisons, let us assume in the following that illuminating gas has a composition like the gas employed by Grashof.<sup>1</sup>

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<sup>1</sup> Grashof, "Theoretische Maschinenlehre." Leipsic, 1875, Vol. 1, p. 907.

In order to facilitate calculation of this sort we will first give, in the following Table *a*, the gas constants belonging to those gases contained in the mixture of the there assumed illuminating gas.

T a b l e a.

	1. Chemical Formula.	2. Molecular Weight. <i>m</i>	3. Constant. <i>B</i>	4. Specific Volume. <i>v</i>	5. Specific <i>c<sub>p</sub></i>	6. Heat. <i>c<sub>v</sub></i>
Marsh gas. . . . .	CH <sub>4</sub>	16	52.824	1.3956	0.5929	0.4680
Ethylene. . . . .	C <sub>2</sub> H <sub>4</sub>	28	30.185	0.7975	0.4040	0.3326
Butylene. . . . .	C <sub>4</sub> H <sub>8</sub>	56	15.092	0.3987	0.4040	0.3326
Hydrogen. . . . .	H <sub>2</sub>	2	422.591	11.1649	3.4090	2.4123
Carbonic oxide. . . . .	CO	28	30.185	0.7975	0.2450	0.1736
Nitrogen. . . . .	N <sub>2</sub>	28	30.185	0.7975	0.2438	0.1727

[ T a b l e a. ]

	1. Chemical Formula.	2. Molecular Weight. <i>m</i>	3. Constant. <i>B</i>	4. Specific Volume. <i>v</i>	5. Specific <i>c<sub>p</sub></i>	6. Heat. <i>c<sub>v</sub></i>
Marsh gas. . . . .	CH <sub>4</sub>	16	96.283	22.356	0.5929	0.4680
Ethylene. . . . .	C <sub>2</sub> H <sub>4</sub>	28	55.018	12.775	0.4040	0.3326
Butylene. . . . .	C <sub>4</sub> H <sub>8</sub>	56	27.508	6.387	0.4040	0.3326
Hydrogen. . . . .	H <sub>2</sub>	2	770.259	178.85	3.4090	2.4123
Carbonic oxide. . . . .	CO	28	55.018	12.775	0.2450	0.1736
Nitrogen. . . . .	N <sub>2</sub>	28	55.018	12.775	0.2438	0.1727

The constants *B* of the equation of condition were calculated from formula (14), p. 105, namely,

$$B = \frac{845.182}{m}$$

$$\left[ B = \frac{1540.52}{m} \right]$$

The specific volume of the several gases is calculated from the equation of condition  $pv = BT$  for 0° C. [32° F.] or  $T = 273^{\circ}$

[ $T=491.4^\circ$ ], and the mean atmospheric pressure  $p=10333$  kg. [2116.3 lb.], with the help of the preceding formula for  $B$ , gives

$$v = \frac{22.3297}{m} \text{ cbm.}$$

$$\left[ v = \frac{357.70}{m} \text{ cu. ft. .} \right]$$

The following Table *b* gives in columns 1, 2, and 3 the constitution of the assumed coal (illuminating) gas, according to the weight and volume of the several gases.

Table *b*.

Kind of Gas.	1. <i>G</i> kg.	2. <i>G<sub>v</sub></i> cbm.	3. <i>V</i> cbm.	4. Oxygen. g kg.	5. Carbonic acid. k kg.	6. Water. w kg.
Marsh gas. . . . .	0.54	0.7536	0.469	4.000	2.750	2.250
Ethylene. . . . .	0.10	0.0797	0.050	3.428	3.143	1.286
Butylene. . . . .	0.08	0.0319	0.020	3.428	3.143	1.286
Hydrogen. . . . .	0.05	0.5582	0.347	8.000	—	9.000
Carbonic oxide. . . . .	0.15	0.1196	0.074	0.571	1.571	—
Nitrogen. . . . .	0.08	0.0638	0.040	—	—	—
	1 kg.	1.6068	1 cbm.			

[Table *b*.]

Kind of Gas.	1. <i>G</i> lb.	2. <i>G<sub>v</sub></i> cu. ft.	3. <i>V</i> cu. ft.	4. Oxygen. g lb.	5. Carbonic acid. k lb.	6. Water. w lb.
Marsh gas. . . . .	0.54	12.072	0.469	4.000	2.750	2.250
Ethylene. . . . .	0.10	1.277	0.050	3.428	3.143	1.286
Butylene. . . . .	0.08	0.511	0.020	3.428	3.143	1.286
Hydrogen. . . . .	0.05	8.942	0.347	8.000	—	9.000
Carbonic oxide. . . . .	0.15	1.916	0.074	0.571	1.571	—
Nitrogen. . . . .	0.08	1.022	0.040	—	—	—
	1 lb.	25.740	1 cu. ft.			

The summation of column 2 gives the volume of 1 kg. [lb.] of the contemplated illuminating gas, i.e., gives its specific volume

$v=1.6068$  [25.740]; its reciprocal value  $\gamma=0.5797$  [ $\gamma=0.03885$ ] gives the specific weight of the gas.

Column 3 gives the several gas quantities in cubic meters [cu. ft.], contained in 1 cbm. [cu. ft.] of illuminating gas. The values are obtained by dividing those of column 2 by 1.6068 [25.740].

In column 4 is given the quantity of oxygen expressed in kilograms [pounds] and designated by  $s$ , which is necessary for the combustion of one kilogram [pound] of the gas in question. It has been calculated, according to the presentation of the preceding article, from the formula

$$s = \frac{2n_1e_3 + 0.5n_2e_3 - n_3e_3}{m} = \frac{32n_1 + 8n_2 - 16n_3}{m} \quad (11)$$

Column 5, designated by  $k$ , gives the weight of the carbonic acid, and column 6, designated by  $w$ , gives the weight of water, developed by the combustion of 1 kg. [lb.] of the gas considered.

The first value is found from the formula

$$k = \frac{n_1(e_1 + 2e_3)}{m} = 44 \frac{n_1}{m}, \quad (12)$$

and the second value from

$$w = \frac{n_2(e_2 + 0.5e_3)}{m} = 9 \frac{n_2}{m} \quad (13)$$

Let us assume that a certain illuminating gas weighing one kilogram [pound] is composed of  $G_1$  kg. [lb.] of marsh gas,  $G_2$  kg. [lb.] of ethylene, etc., also let the values in columns 3 to 6 be designated by the letters of the headings and by the subscripts 1, 2, etc.; then the constant  $B$  of the equation of condition of this illuminating gas can be computed with the help of the formula

$$B_g = \Sigma(GB), \quad (14)$$

where  $B_g$  is employed to avoid confusion. Similarly the amount of oxygen  $s$ , necessary for combustion of 1 kg. [lb.], and the carbonic acid and water resulting from the combustion can be found, respectively, from

$$s = \Sigma(Gs), \quad k = \Sigma(Gk), \quad \text{and} \quad w = \Sigma(Gw) \quad (15)$$

and finally the specific heat of this illuminating gas for constant pressure and constant volume respectively is

$$c_p = \Sigma(Gc_p) \text{ and } c_v = \Sigma(Gc_v). \quad . \quad . \quad . \quad . \quad (16)$$

For butylene there are no observations on its specific heat, and therefore the ethylene values were substituted for it.

For our coal (illuminating) gas (Table b, p. 412) we get, with the help of the preceding formulas and the numerical values, for the constant of the equation of condition

$$B_g = 60.823 \\ [B_g = 110.86].$$

Further we find for the oxygen requisite for 1 kg. [lb.] of illuminating gas the quantity  $s = 3.262$  kg. [lb.], for the produced carbonic acid  $k = 2.286$  kg. [lb.], and for the quantity of water  $w = 1.896$ .

Finally there is found

$$c_p = 0.6196, \quad c_v = 0.4730, \quad \kappa = \frac{c_p}{c_v} = 1.310.$$

Now if the gas considered is mixed with  $q$  kg. [lb.] of air, and  $V$  is the volume of this air, then its equation of condition can be written

$$Vp = qB_iT,$$

where, for air, we have  $B_i = 29.269$  [53.349] (see p. 104); on the other hand, for the unit of weight of gas we have

$$pv = B_gT.$$

Consequently for equal pressure and equal temperature we have the ratio of the air volume to the volume of the illuminating gas under consideration:

$$\frac{V}{v} = 0.481q. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Since 1 kg. [lb.] of air contains  $\alpha = 0.2356$  kg. [lb.] of oxygen, we determine the minimum quantity of air necessary for combustion from  $q\alpha = s$ , or

$$q = 13.85 \text{ kg.},$$

from which the minimum of the air volume,  $V = 6.66 v$ , results.

If the contemplated gas is mixed with  $q$  kg. [lb.] atmospheric air, where  $q > 13.85$ , then we find for the mixture before ignition

$$B_m = \frac{60.823 + 29.269 q}{q + 1} \quad \left[ B_m = \frac{110.86 + 53.349 q}{q + 1} \right],$$

also

$$c_p' = \frac{0.6196 + 0.2375 q}{q + 1} \quad \text{and} \quad c_v' = \frac{0.4730 + 0.1685 q}{q + 1}.$$

On the other hand, after combustion we have

$$B = \frac{48.984 + 29.269 q}{q + 1} \quad \left[ B = \frac{89.284 + 53.345 q}{q + 1} \right],$$

also

$$c_p = \frac{0.7169 + 0.2375 q}{q + 1} \quad \text{and} \quad c_v = \frac{0.6011 + 0.1685 q}{q + 1},$$

because here we have on hand 2.286 kg. [lb.] of carbonic acid, 1.896 kg. [lb.] of water,  $(0.2356q - 3.262)$  kg. [lb.] of oxygen, and  $(0.7644 q + 0.08)$  kg. [lb.] of nitrogen, and because the constants, given on p. 406, are used.

For example there follows from this, for the minimum quantity of air  $q = 13.85$  kg. [lb.] before combustion,

$$B_m = 31.394 \quad [B_m = 57.222], \quad c_p' = 0.2632, \quad c_v' = 0.1890, \quad \frac{c_p'}{c_v'} = 1.392;$$

after combustion,

$$B = 30.597 \quad [B = 55.769], \quad c_p = 0.2698, \quad c_v = 0.1976, \quad \frac{c_p}{c_v} = 1.365.$$

These last results of calculation lead to propositions which greatly facilitate and simplify the computations connected with gas engines. Although the combustion of our illuminating gas presupposes the minimum quantity of air, nevertheless the physical constants before and after ignition are of nearly

equal magnitude; with a greater quantity of air the equality is still more apparent.

If we consider that some of the values introduced into the calculation are not yet certainly established experimentally, we may for the present, in technical calculations, assume:

1. that combustion of illuminating gas in a gas engine, after a preliminary mixing with atmospheric air, involves no change of volume provided the mixture, after combustion, is brought back to the initial pressure and initial temperature, and that the water generated is present in the gaseous state;

2. that the specific heat both for constant pressure and constant volume may be taken as equal before and after combustion, and its determination can be obtained from the proportions of the mixture before ignition; finally

3. that the values thus calculated are also valid in the case in which the illuminating gas is not only mixed with atmospheric air, but also with gases left over from a preceding combustion.

These propositions, however, only hold under the express assumptions maintained for the present that the specific heats  $c_p$  and  $c_v$  of the gases are independent of pressure and temperature.

### § 73. THE HEATING VALUE OF COMBUSTIBLE GASES.

For the purpose of technical investigations of the present kind it is permitted to utilize the experimental results of Favre and Silbermann on the heating value of combustible gases, although the extensive and later investigations of Berthelot and J. Thomsen have far surpassed those older ones; for the gases here considered, however, the discrepancies are but slight.

Favre and Silbermann observed for these gases the heat quantity  $W$  released when one kilogram [pound] of the gas was burned in the calorimeter.

The experimental values of  $W$  are given in column 2 of the following table:

Table.

1.	2. <i>W</i> cal.	3. <i>H</i> cal.	4. <i>H</i> <sub>1</sub> cal.	5. <i>H</i> <sub>2</sub> <sup>(1)</sup> cal.
Marsh gas, CH <sub>4</sub> .....	13063	11710	2930	2342
Ethylene, C <sub>2</sub> H <sub>4</sub> .....	11858	11090	3235	2504
Butylene, C <sub>4</sub> H <sub>8</sub> .....	?	10840	3162	2447
Hydrogen, H <sub>2</sub> .....	34462	29060	3630	3229
Carbonic oxide, CO.....	2403	2400	2100	1528

[ Table.]

1.	2. <i>W</i> B.t.u.	3. <i>H</i> B.t.u.	4. <i>H</i> <sub>1</sub> B.t.u.	5. <i>H</i> <sub>2</sub> B.t.u.
Marsh gas, CH <sub>4</sub> .....	23513	21078	5274	4216
Ethylene, C <sub>2</sub> H <sub>4</sub> .....	21344	19962	5823	4507
Butylene, C <sub>4</sub> H <sub>8</sub> .....	?	19512	5692	4405
Hydrogen, H <sub>2</sub> .....	62032	52308	6534	5812
Carbonic oxide, CO.....	4325	4320	3780	2750

It is to be noted that the experimental values given by Favre and Silbermann do not represent the real heating values. Since the gases were burned in the calorimeter at constant atmospheric pressure, and then cooled to the initial (atmospheric) temperature, the steam generated was, in so doing, almost completely condensed; the calorimeter thus withdrew from it a certain heat quantity which is contained in the value *W* and should be subtracted from it, in order to determine the real heating power *H*.

Now, as later investigations will show, the quantity of heat which must be withdrawn from one kilogram [pound] of saturated steam at atmospheric temperature, in order to convert it under constant pressure into water, amounts to about 600 cal. [1080 B.t.u.] in round numbers; therefore if the combustion of

<sup>1</sup> The values given in the table for *H*<sub>2</sub> differ but slightly from the values which Berthelot found (Ann. de chim. et de phys., 4th Series, Vol. 22, p. 130).



1 kg. [lb.] of gas generates  $w$  kg. [lb.] of steam, the heat quantity under consideration is  $600 w$  [1080  $w$ ] and there consequently follows

$$H = W - 600 w \text{ [} H = W - 1080 w \text{]}.$$

For the gases given in the preceding table the corresponding values of  $w$  are given in the table on p. 412; thus the heating values  $H$  given in column 3 can be calculated and the results agree with *Grashof's* data; the value given for butylene gas was estimated by *Grashof*.

If we suppose the combustion to be effected by pure oxygen and if we divide the heating power  $H$  by the weight  $s$  of the oxygen assigned to 1 kg. [lb.] of gas (see table, p. 412) we get the values  $H_1$  given in column 4 of the preceding table. (With carbonic oxide gas the divisor was  $2 \times 0.571$ .)

These values give the heat quantities per kg. [lb.] of oxygen. *Welter* concluded from the older experiments of *Lavoisier* and *Rumford* that equal heat quantities must correspond to equal quantities of oxygen; the values of  $H_1$  ought therefore to be of nearly the same magnitude; we see, however, that *Welter's* proposition is not confirmed and this has been pointed out before.

On the other hand if the heating power is referred to 1 kg. [lb.] of mixture of gas and oxygen we get the values  $H_2$  of column 5; they were found from the division of  $H$  by  $(k+w)$  or by  $1+s$ , the latter values being taken from the table on p. 412.

It follows therefore that

$$H_2 = \frac{H}{1+s}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

We see that the values  $H_2$  also follow no simple law.

Let us consider a mixture of combustible gases (illuminating gas) and designate the gas-weights contained in a unit of weight of mixture, as before, by  $G_1, G_2$ , etc., and their heating power  $H$  (taken from column 3 of the preceding table) by  $H_1, H_2, H_3$ , etc., then the heating power of this mixture is determined by

$$H = \Sigma(GH). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

For example, in the illuminating gas, assumed on p. 412, we have

$$H = 10113 \text{ cal. [18203 B.t.u.].}$$

According to the investigations in § 24, p. 132, the heat contents  $J$  of the unit of weight of a gas, or of its inner work  $U$ , expressed in units of heat, is given by

$$J = J_0 + c_v T,$$

where  $J_0$  is a constant belonging to the gas in question; in what follows let  $J$  be simply called the "gas heat" and  $J_0$  the "constant of the gas heat." This constant can be found for the unit of weight of a mixture of different gases from equation (18), p. 175,

$$J_0 = \Sigma(GJ_0), \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where  $G_1, G_2, G_3, \dots$  represent the weights of the several gases, and  $J_0', J_0'', J_0''', \dots$  their constants.

Now for a mixture of one kilogram [pound] of combustible gases let  $J_1$  be the constant of the gas heat,  $c_1$  the specific heat at constant volume for this mixture,  $B_1$  the constant of the equation of condition; moreover let these same magnitudes for the mixture after combustion be designated by  $J_2, c_2$ , and  $B_2$  respectively; let pressure, volume, and temperature before ignition be  $p_1, v_1$ , and  $T_1$ , after combustion  $p_2, v_2$ , and  $T_2$ ; then the process of combustion can be represented, in a general fashion, by the curve  $ACB$ , Fig. 63, which I have called the "combustion curve." The points  $A$  and  $B$  represent the gas condition before and after combustion, and if, during combustion, pressure and volume have changed according to the course of the arbitrary curve  $AB$ , then in so doing a work  $L$  is produced, which is represented by the area  $V_1ABV_2$ . If the combustion takes place without heat supply from, and without heat withdrawal by, the outside, then evidently the gas heat at the end is equal to that at the

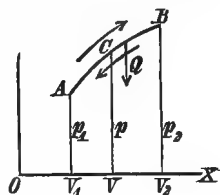


FIG. 63.

beginning, diminished by the heat quantity converted into work, and therefore

$$J_2 + c_2 T_2 = J_1 + c_1 T_1 - AL,$$

from which follows

$$J_1 - J_2 = c_2 T_2 - c_1 T_1 + AL, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and at the same time the relations

$$p_1 v_1 = B_1 T_1 \quad \text{and} \quad p_2 v_2 = B_2 T_2 \quad . \quad . \quad . \quad . \quad . \quad (22)$$

hold.

Let the mixture of gases be led back by the same, but reversed, path *BA* to the initial values of  $p_1$  and  $v_1$ . The heat quantity  $Q$ , which must be withdrawn in so doing, is found from

$$Q = c_2(T_2 - T) + AL, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where  $T$  is the temperature of the mixture at the point *A*, after the return.

Combination of equation  $p_1 v_1 = B_2 T$  with the first of equations (22) gives

$$T = \frac{B_1}{B_2} T_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Utilization of this expression and elimination of  $AL$  from the two equations (21) and (23) give

$$J_1 - J_2 = Q + \frac{c_2 B_1 - c_1 B_2}{B_2} T_1 \quad . \quad . \quad . \quad . \quad . \quad (25)$$

In Favre and Silbermann's experiments the here-described procedure actually occurred, only the combustion and return took place at constant pressure  $p_1$  and so the curve *AB* was a horizontal straight line.

The value here designated by  $Q$  is identical with the value  $H_2$ , column 5, for the gases adduced in the table on p. 417, and for these gases the difference  $J_1 - J_2$  can be computed,  $T_1$  being assumed as the mean atmospheric temperature, because from the known proportions of the mixture before and after combustion, the values  $c_1$  and  $c_2$  and also  $B_1$  and  $B_2$  can be determined. Under the hypothesis that the gas considered burns with pure oxygen, and assuming the data in the table on p. 412, and considering the data already given, we get the values given in the following tabulation.

## T a b u l a t i o n.

	$c_1$	$c_2$	$B_1$	$B_2$	$J_1 - J_2$
Marsh gas. . . . .	0.2177	0.2607	31.74	31.74	2355
Ethylene. . . . .	0.1952	0.2292	27.31	27.31	2514
Butylene. . . . .	0.1952	0.2292	39.90	27.27	2449
Hydrogen. . . . .	0.4059	0.3695	70.42	46.95	3272
Carbonic oxide. . . . .	0.1669	0.1718	28.80	19.20	1551

## [T a b u l a t i o n.]

	$c_1$	$c_2$	$B_1$	$B_2$	$J_1 - J_2$
Marsh gas. . . . .	0.2177	0.2607	57.720	57.720	4239
Ethylene. . . . .	0.1952	0.2292	49.778	49.778	4525
Butylene. . . . .	0.1952	0.2292	72.726	49.705	4408
Hydrogen. . . . .	0.4059	0.3695	128.355	85.576	5890
Carbonic oxide. . . . .	0.1669	0.1718	52.494	34.996	2792

The values  $J_1 - J_2$  of the last column are computed from equation (25) for the mean temperature  $t_1 = 20^\circ \text{C}$ . [ $68^\circ \text{F}$ .], i.e.,  $T_1 = 293^\circ \text{C}$ . [ $527.4^\circ \text{F}$ .] and differ but little from the values  $H_2$ , p. 417.

In the difference  $(J_1 - J_2)$ , we repeat, the first term  $J_1$  represents the constant of the gas heat for the mixture of the combustible gas with pure oxygen, and  $J_2$  refers to the mixture after combustion, consisting of carbonic acid and water.

Now if we represent this constant for the gas in question by  $J_0$ , and its value for oxygen, carbonic acid, and water respectively  $J_s$ ,  $J_k$ , and  $J_w$ , then, according to equation (19), the following relations:

$$\left. \begin{aligned} (1+s)J_1 &= J_0 + sJ_s, \\ (1+s)J_2 &= kJ_k + wJ_w, \end{aligned} \right\} \dots \dots \dots (26)$$

hold, when, as was assumed in calculating the table on p. 412,  $s$  kg. [lb.] of oxygen are furnished for 1 kg. [lb.] of gas, and when the result is  $k$  kg. [lb.] of carbonic acid and  $w$  kg. [lb.] of water.

The difference then gives for the gas considered

$$J_0 = (1+s)(J_1 - J_2) + kJ_k + wJ_w - sJ_s. \dots \dots (27)$$

If, therefore, the values  $J_k$ ,  $J_w$ , and  $J_s$  were known, the constant  $J_0$  could be computed for all gases of the composition

( $C_{n_1}H_{n_2}O_{n_3}$ ). As regards this problem only one experiment exists for its solution, which is by *Nordenskiöld*<sup>1</sup>; from the experimental results of *Favre* and *Silbermann* on the heats of combustion of organic fluids of the preceding composition there were found the following values for this constant  $J_0$ :

for Oxygen:  $J_s = 7317$  cal. [13170.6 B.t.u.],

Carbonic acid:  $J_k = 4312$  cal. [7761.6 B.t.u.],

Vapor of water:  $J_w = 7275$  cal. [13095 B.t.u.],

of course under the hypothetical proviso that the heats of combustion of these fluids are inversely proportional to their specific weights.

With the help of these values and the corresponding values  $s$ ,  $k$ , and  $w$  in Table b, p. 412, we can compute from equations (26) the following tabulation.

Combustible Gas.	Gas Heat Constants.		
	$J_2$	$J_1$	$J_0$
Marsh gas. . . . .	5645	8000	10732
Ethylene. . . . .	5173	7687	8955
Butylene. . . . .	5173	7622	8667
Hydrogen. . . . .	7275	10547	36387
Carbonic oxide. . . . .	4312	5863	5033

[Table.]

Combustible Gas.	Gas Heat Constants.		
	$J_2$	$J_1$	$J_0$
Marsh gas. . . . .	10161	7200	19318
Ethylene. . . . .	9311	13837	16119
Butylene. . . . .	9311	13720	15601
Hydrogen. . . . .	13095	18985	65497
Carbonic oxide. . . . .	7762	10553	9059

<sup>1</sup> *Poggendorff's Annalen*, Vol. 109, 1860, p. 184.—*Wüllner*, *Lehrbuch der Experimentalphysik*, Vol. 3.

The contents  $J_2$  are computed from formula (26):

$$(1+s)J_2 = kJ_k + wJ_w,$$

while  $J_1$  results from the relation

$$J_1 = J_2 + (J_1 - J_2),$$

where the corresponding values  $J_1 - J_2$  are taken from the table on p. 421.

The values  $J_0$  are computed according to the first of equations (26):

$$J_0 = (1+s)J_1 - sJ_s.$$

Moreover we may especially emphasize that  $J_2$  is the constant of the gas heat after the combustion of the gas with pure oxygen, while  $J_1$  is the constant of the mixture of the combustible gas with the necessary oxygen before combustion.  $J_0$  is the constant for the combustible gas considered.

The value  $J_0$  could therefore also be calculated for every mixture of the gases here given.

An exact determination of the quantities considered would certainly be of importance for the further development of thermodynamics; for the present the values given by Norden skiöld and the values just derived from them must be regarded as hypothetical.

## § 74. THERMODYNAMIC EQUATIONS FOR THE PROCESS OF COMBUSTION OF A GAS WITH INVARIABLE SPECIFIC HEATS.

If the unit of weight of a combustible gas is mixed with  $s$  kg. [lb.] of oxygen, i.e., with just enough of it to effect perfect combustion, and if the products consist of  $k$  kg. [lb.] of carbonic acid and  $w$  kg. [lb.] of water, then, at a particular instant, say at the point  $C$  of the combustion curve  $AB$  (Fig. 63, p. 419), in which  $x$  kg. [lb.] of gas have just been burned, the total weight  $1+s = (k+w)$  kg. [lb.] of the gas mixture will consist of  $(1-x)$  kg. [lb.] of gas,  $(1-x)s$  kg. [lb.] of oxygen,  $kx$  kg. [lb.] of carbonic acid,

and  $wx$  kg. [lb.] of steam; the specific heat  $c_x$  at constant volume for this mixture can be calculated in the manner given, also the constant  $B_x$  of the equation of condition, and finally from this equation itself the temperature can be computed for every given value of the pressure  $p$  and volume  $v$ .

The constant  $J_x$  for the gas heat of the mixture can be determined, provided  $J_0$  is the constant for the combustible gas itself, from the relation

$$(1+s)J_x = (1-x)J_0 + (1-x)sJ_s + kxJ_k + wxJ_w,$$

or

$$(1+s)J_x = J_0 + sJ_s + (kJ_k + wJ_w)x - (J_0 + sJ_s)x,$$

or, taking into consideration equations (26),

$$J_x = J_1 - (J_1 - J_2)x. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

This formula also holds when there is mixed with the combustible gas, at the beginning, not only oxygen, but also an indifferent (neutral) gas; enough oxygen must be on hand, however, to burn the whole gas; any excess of oxygen would have to be counted with the indifferent gas; if  $i$  kg. [lb.] of such a gas were on hand and  $J_i$  its constant, we should write in place of equations (26)

$$\left. \begin{aligned} (1+s+i)J_1 &= J_0 + sJ_s + iJ_i, \\ (1+s+i)J_2 &= kJ_k + wJ_w + iJ_i. \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad (29)$$

For the considered point  $C$  of the combustion curve  $AB$  (Fig. 63, p. 419) there can be found, in the same way, the specific heat  $c_x$  at constant volume, also the constant  $B_x$  of the equation of condition:

$$c_x = c_1 - (c_1 - c_2)x, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

$$B_x = B_1 - (B_1 - B_2)x, \quad . \quad . \quad . \quad . \quad . \quad (31)$$

and for the equation of condition of the mixture at this instant

$$pv = [B_1 - (B_1 - B_2)x]T \quad . \quad . \quad . \quad . \quad . \quad (32)$$

for the corresponding temperature  $T$ .

Taking a unit of weight of a gas mixture, the heat content at the point  $C$  of the curve  $AB$  is given by  $J_x + c_x T$ ; on the other hand, for the beginning, it is given by  $J_1 + c_1 T_1$ ; the difference gives the increment of the heat content when equations (28) and (30) are used:

$$c_1(T - T_1) - [J_1 - J_2 + (c_1 - c_2)T]x.$$

The bracketed quantity designated by  $\rho$  is a simple function of the temperature because the constant quantities  $J_1$ ,  $J_2$ ,  $c_1$ , and  $c_2$  are known for the case in hand, i.e., substitute

$$\rho = J_1 - J_2 + (c_1 - c_2)T, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

and we shall get for the total increase

$$c_1(T - T_1) - \rho x.$$

Now if during combustion, i.e., during the corresponding chemical change, there is also supplied to the mass, from without, the heat quantity  $Q$  along the path  $AC$  of the curve  $AB$ , and if in so doing the external work  $AL$  is produced, then the relation

$$Q = c_1(T - T_1) - \rho x + AL$$

obtains, or, passing to the differential,

$$dQ = c_1 dT - d(\rho x) + A p dv, \quad . \quad . \quad . \quad . \quad . \quad (34)$$

where the function  $\rho$  is given by equation (33).

The preceding equation is the result of an attempt to extend the fundamental equation of thermodynamics for gases to the case in which there exist simultaneously chemical equations of condition. If combustion did not take place during heat supply, then  $x$  would be 0 and constant; then we should again obtain the equation as it was presented on p. 134. In its structure, moreover, the preceding formula is identical with the one which subsequent investigations will furnish for the heat quantity that is necessary for the evaporation of liquids.

The preceding investigations exist in the earlier edition of this book (1887, Vol. I, p. 413). Recently Stodola in the article



“Die Kreisprozesse in der Gasmaschine,” Zeitschrift des Vereins deutscher Ingenieure (Vol. 42, 1898, pp. 1045 and 1086), has given for the process of combustion equations which agree in structure with the formulas given above in the text, and for gases in particular are identical with them. More recently still H a n s L o r e n z in “Technische Wärmelehre,” 1904, p. 392, has derived the same equations for gases in a somewhat different form, but extends the investigations, like S t o d o l a, to the case of variable specific heats in accordance with the experimental results of M a l l a r d and L e C h a t e l i e r, a supposition which we will likewise make later on.

**Example.** H y d r o g e n d e t o n a t i n g g a s, a mixture of hydrogen and oxygen in the proportion in which the two gases unite to form water, is to be burned at constant volume. Let  $p_1$  and  $T_1$  be the pressure and temperature of the mixture at the beginning, and let  $p_2$  and  $T_2$  be the pressure and temperature at the end of combustion, in the state of vapor; then, because  $v_2 = v_1$ , we find from equations (22)

$$\frac{p_2}{p_1} = \frac{B_2 T_2}{B_1 T_1}, \quad . . . . . (\alpha)$$

when perfect combustion obtains, i.e.,  $x=1$ , while at the beginning  $x=0$ . From the integration of equation (34) there follows here, because  $dv=0$ ,

$$Q = c_1(T_2 - T_1) - p_2,$$

and with equation (33)

$$Q + J_1 - J_2 = c_2 T_2 - c_1 T_1, \quad . . . . . (\beta)$$

where  $Q$  represents the quantity of heat which must be supplied from without during the process of combustion.

During the explosion heat is neither supplied nor withdrawn, i.e., let  $Q=0$ . If the initial temperature of the mixture is  $t_1=20^\circ$  [ $68^\circ$  F.] and  $T_1=293^\circ$  [ $527.4^\circ$  F.], and if we utilize the constants  $B_1$ ,  $B_2$ , etc., given for hydrogen in the tabulation on p. 421, there will result from equations ( $\alpha$ ) and ( $\beta$ )

$$T_2 = 9177^\circ, \quad t_2 = 8904^\circ, \quad \text{and} \quad \frac{p_2}{p_1} = 20.88$$

$$[T_2 = 16518.6, \quad t_2 = 16059.2].$$

B u n s e n found, by experiments, that the pressure ratio  $\frac{p_2}{p_1} = 9.6$  obtained; here therefore are conditions which still require explanation. The most natural and probably the most correct idea is, that dissocia-

tion (see p. 91) must here play an important part;<sup>1</sup> for does not the calculation in the preceding example give the enormously high temperature of combustion  $t_2 = 8904^\circ \text{C.}$  [ $16060^\circ \text{F.}$ ]?

As a special case we will discuss gas combustion at constant temperature.

If the constant value of the combustion temperature is designated by  $T$ , then the value of  $\rho$ , from equation (33), namely,

$$\rho = J_1 - J_2 + (c_1 - c_2)T, \dots \dots \dots (35)$$

is constant, and because  $dT = 0$ , equation (34) gives

$$dQ = -\rho dx + A\rho dv.$$

But the differentiation of equation (32) gives

$$d(pv) = -(B_1 - B_2)Tdx.$$

If we determine  $dx$  from this, we get

$$dQ = \frac{\rho}{(B_1 - B_2)T} d(pv) + A\rho dv.$$

It for simplification we substitute

$$m = 1 + \frac{A(B_1 - B_2)T}{\rho}, \dots \dots \dots (36)$$

there follows, after simple reduction,

$$dQ = \frac{A\rho v}{m-1} d \log_e (pv^m). \dots \dots \dots (37)$$

Therefore according to the method of heat supply the isothermal curve of combustion will have a different course.

If, during combustion, heat is neither supplied nor withdrawn,

<sup>1</sup> Mallard and Le Chatelier found that a noticeable dissociation did not occur as long as the temperature of carbonic acid was below  $1800^\circ$  ( $3240^\circ \text{F.}$ ) and as long as the temperature of steam was below  $2000^\circ$  [ $3600^\circ \text{F.}$ ]. *Annales des Mines*, Vol. IV, 1883, p. 456.

then  $dQ=0$ , and from equation (37) follows for the course of the combustion curve

$$pv^m = p_1 v_1^m, \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where  $m$  is to be determined with the help of equations (35) and (36).

For example, we find for detonating gas, which is to burn at the constant temperature  $t=500^\circ \text{C.}$  [ $932^\circ \text{F.}$ ] or  $T=773^\circ$  [ $1391.4^\circ$ ] for the exponent  $m$ ,

$$m=1.13,$$

from the values given for hydrogen in the tabulation on p. 421. On the other hand for gases or gas mixtures, in which the gas constants are taken equally large before and after combustion, i.e., for which we substitute  $B_1=B_2$ , we find  $m=1$ ; the isothermal curve of combustion is then the isothermal of ordinary gases, i.e., an equilateral hyperbola.

## § 75. THE FUNDAMENTAL EQUATIONS AND THE EQUATIONS FOR THE COMBUSTION PROCESS OF GASES WITH VARIABLE SPECIFIC HEAT.

If we continue to hold fast to the assumption that gases are subject to the ordinary equation of condition  $pv=BT$ , we find, as was shown on p. 145, that the specific heat at constant pressure can only be a function of the temperature, but that its difference from the specific heat at constant volume again appears as a constant and that the equation

$$c_p - c_v = AB$$

is here also valid.

Now if we substitute

$$c_v = c_0 + \tau \quad \text{and} \quad c_p = k_0 c_0 + \tau, \quad . \quad . \quad . \quad (39)$$

where  $\tau$  represents any temperature function and the quantities  $c_0$  and  $k_0$  are regarded as constants still to be determined, then

in place of equation (51a), p. 132, there may be written for the variation of energy of a gas for any change of state whatsoever

$$dJ = AdU = (c_0 + \tau)dT, \quad . \quad . \quad . \quad . \quad . \quad (40)$$

and for the supplied heat quantity  $dQ$  there is found

$$dQ = (c_0 + \tau)dT + Apdv, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

which equation, like the one (53), p. 133, can be written in different forms. It results that at constant temperature or constant energy the isothermal curve, and the isodynamic, can be represented by an hyperbola. The circumstances are different, however, with the adiabatic curve, and as this is of importance right here, because of the course of expansion in gas engines, it will be examined more closely. In so doing the propositions of Mallard and Le Chatelier will at once be applied. Accordingly the temperature function  $\tau$  is represented by  $\alpha_0 T$ , where  $\alpha_0$  is a constant, valid for the gas considered. (See equations ( $\gamma$ ) upon p. 147.) We therefore write in place of equation (40)

$$AdU = dJ = (c_0 + \alpha_0 T)dT \quad . \quad . \quad . \quad . \quad . \quad (42)$$

and

$$dQ = (c_0 + \alpha_0 T)dT + Apdv. \quad . \quad . \quad . \quad . \quad (43)$$

The difference of equations (39) gives

$$c_p - c_v = (k_0 - 1)c_0 = AB. \quad . \quad . \quad . \quad . \quad . \quad (44)$$

If we utilize this relation and divide both sides of equation (43) by  $AT$ , then there is found for the differential of entropy  $P$ ,

$$AdP = c_0 d(\log_e pv^{k_0}) + \frac{\alpha_0}{c_0} \frac{Ad(pv)}{k_0 - 1},$$

and from this, by integration,

$$AP = c_0 \log_e (pv^{k_0}) + \frac{\alpha_0}{c_0} \frac{Apv}{k_0 - 1} + AP_0. \quad . \quad . \quad . \quad (45)$$

But for the adiabatic curve the entropy is the same for all points, and we therefore get for this curve the equation

$$c_0 \log_e (pv^{k_0}) + \frac{\alpha_0}{c_0} \frac{Apv}{k_0 - 1} = \text{Constant.} \quad . \quad . \quad . \quad (46)$$

Compare this with equation (59), p. 139, with respect to the ordinary case of invariable specific heat at constant volume. Closer investigation shows that according to this equation (46) the adiabatic approaches the axis of abscissas less rapidly than in the case treated on p. 139; it approaches more to the isothermal curve, which is, in general, confirmed by the indicator diagrams of gas engines.

Since equation (39) represents the specific heat at constant volume as

$$c_v = c_0 + \alpha_0 T$$

the constants  $c_0$  and  $\alpha_0$  are found from equations (7), p. 147, when we divide their two members by the molecular weight  $m$  (according to data on p. 147) to be as follows:

	$c_0$	$\alpha_0$ (C.)	$[\alpha_0$ (F.)]
Hydrogen, $H_2$ . . . . .	2.047	0.00122	0.000678
Oxygen, $O_2$ . . . . .	0.128	0.000076	0.0000422
Nitrogen, $N_2$ . . . . .	0.146	0.000087	0.0000483
Carbonic oxide, $CO$ . . .	0.146	0.000087	0.0000483
Steam, $H_2O$ . . . . .	0.234	0.000318	0.000177
Carbonic acid, $CO_2$ . . .	0.100	0.000176	0.0000978

To these preliminary investigations we now add the investigations concerning the combustible process of gases with variable specific heat.

Let the unit of weight of a combustible gas be mixed with  $s$  kg. [lb.] of oxygen and  $i$  kg. [lb.] of an indifferent (neutral) gas. The total weight  $G$  of the gas mixture is therefore

$$G = 1 + s + i. \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Now let the constant  $B$  of the equation of condition  $pv = BT$  for the combustible gas be  $B_0$ , for oxygen be  $B_s$ , for the indifferent gas be  $B_i$ ; in like manner we have for carbonic acid  $B_k$  and for the vapor of water  $B_w$ , provided, after complete combustion,  $k$  kg. [lb.] of carbonic acid and  $w$  kg. [lb.] of steam are on hand.

Now suppose that at the point  $C$  of the combustion curve, Fig. 63, p. 419, just  $x$  kg. [lb.] of combustible gas have been burnt; let  $V$  be the total volume of the gas mixture and let the partial pressures be respectively represented by  $p_0$ ,  $p_i$ ,  $p_s$ ,  $p_k$ , and  $p_w$ , and their sum by  $p$ , and then the following relations obtain:

$$\begin{aligned} p_0 V &= (1-x)B_0 T, \\ p_i V &= iB_i T, \\ p_s V &= (1-x)sB_s T, \\ p_k V &= xkB_k T, \\ p_w V &= xwB_w T, \end{aligned}$$

and from them follows, by addition,

$$\frac{Vp}{T} = (B_0 + iB_i + sB_s) - x(B_0 + sB_s - kB_k - wB_w). \quad (48)$$

If we introduce the specific volume  $v$ , we have

$$V = Gv = (1 + s + i)v,$$

and equation (48) gives for the beginning of the combustion, i.e., for  $x=0$ , the constant  $B_1$  of the equation of condition,

$$B_1 = \frac{B_0 + iB_i + sB_s}{1 + s + i}, \quad (49)$$

and likewise  $B_2$  for the end of the combustion, i.e., for  $x=1$ ,

$$B_2 = \frac{kB_k + wB_w + iB_i}{1 + s + i}. \quad (50)$$

The difference gives

$$(1 + s + i) (B_1 - B_2) = B_0 + sB_s - kB_k - wB_w,$$

hence there follows, according to equation (48), the simple relation

$$\frac{pv}{T} = B_1 - (B_1 - B_2)x, \quad \dots \quad (51)$$

in which  $B_1$  and  $B_2$  are given by equations (49) and (50). Equation (51) is identical with equation (32), p. 424.

For a single gas we get, according to equation (42), p. 429, for the variation of energy measured in units of heat,

$$AdU = dJ = (c_0 + \alpha_0 T) dT,$$

and from this, by integration,

$$J = J_0 + c_0 T + \frac{1}{2} \alpha_0 T^2, \quad \dots \quad (52)$$

where  $J_0$  is again the "constant of the gas heat."

Let the total weight  $G$  of the  $V$  mixture be  $G = 1 + s + i$  and again designate the constants of the preceding equation of the several gases of this mixture by subscripts  $i$ ,  $s$ ,  $k$ , and  $w$  respectively; then the heat constant  $GJ$  for the point  $C$  of the combustible curve, Fig. 63, p. 419, is

$$\begin{aligned} GJ = & (1-x)(J_0 + c_0 T + \frac{1}{2} \alpha_0 T^2) + i(J_i + c_i T + \frac{1}{2} \alpha_i T^2) \\ & + (1-x)s(J_s + c_s T + \frac{1}{2} \alpha_s T^2) \\ & + xk(J_k + c_k T + \frac{1}{2} \alpha_k T^2) \\ & + xw(J_w + c_w T + \frac{1}{2} \alpha_w T^2). \end{aligned}$$

From this, by addition and transformation of the terms,

$$\left. \begin{aligned} GJ = & (J_0 + iJ_i + sJ_s) + (c_0 + ic_i + sc_s)T \\ & + (\frac{1}{2} \alpha_0 + \frac{1}{2} i \alpha_i + \frac{1}{2} s \alpha_s) T^2 - (J_0 + sJ_s - kJ_k - wJ_w)x \\ & - (c_0 + sc_s - kc_k - wc_w)xT \\ & - (\frac{1}{2} \alpha_0 + \frac{1}{2} s \alpha_s - \frac{1}{2} k \alpha_k - \frac{1}{2} w \alpha_w)xT^2. \end{aligned} \right\} \quad (53)$$

Introducing the following notation for simplification:

$$J_0 + sJ_s + iJ_i = GJ_1, \quad \dots \quad (54)$$

$$iJ_i + kJ_k + wJ_w = GJ_2, \quad \dots \quad (55)$$

$$c_0 + sc_s + ic_i = Gc_1, \quad . \quad . \quad . \quad . \quad . \quad (56)$$

$$ic_i + kc_k + wc_w = Gc_2, \quad . \quad . \quad . \quad . \quad . \quad (57)$$

$$\alpha_0 + s\alpha_s + i\alpha_i = Gh_1, \quad . \quad . \quad . \quad . \quad . \quad (58)$$

$$i\alpha_i + k\alpha_k + w\alpha_w = Gh_2, \quad . \quad . \quad . \quad . \quad . \quad (59)$$

we finally get, in place of equation (53),

$$J = J_1 + c_1T + \frac{1}{2}h_1T^2 - [J_1 - J_2 + (c_1 - c_2)T + \frac{1}{2}(h_1 - h_2)T^2]x.$$

We designate the bracketed expression by  $\rho$ , that is, if we make

$$[J_1 - J_2 + (c_1 - c_2)T + \frac{1}{2}(h_1 - h_2)T^2] = \rho, \quad . \quad . \quad . \quad (60)$$

there follows

$$J = J_1 + c_1T_1 + \frac{1}{2}h_1T^2 - x\rho \quad . \quad . \quad . \quad . \quad (61)$$

for any corresponding stage of combustion and, from this, by differentiation,

$$AdU = dJ = c_1dT + h_1TdT - d(x\rho). \quad . \quad . \quad . \quad (62)$$

The last equations refer to the unit of weight of the whole gas mixture.

If combustion takes place under heat supply, we get the fundamental formula

$$dQ = c_1dT + h_1TdT - d(x\rho) + Apdv, \quad . \quad . \quad . \quad (63)$$

which, with the help of the equation of condition and equation (51), permits different transformations.

**Example.** Hydrogen detonating gas, a mixture of hydrogen and oxygen in the ratio in which the two gases unite to form water, is to be burnt at constant volume.

Let  $T_1$  be the initial and  $T_2$  the final temperature; then for complete combustion  $x=1$  and we get from equation (63)

$$Q = c_1(T_2 - T_1) + \frac{1}{2}h_1(T_2^2 - T_1^2) - \rho_2, \quad . \quad . \quad . \quad . \quad (63a)$$

in which, according to equation (60), we must substitute

$$\rho_2 = J_1 - J_2 + (c_1 - c_2)T_2 + \frac{1}{2}(h_1 - h_2)T_2^2 \quad . \quad . \quad . \quad (60a)$$



Now here  $s=8$ ,  $w=9$ , and therefore, using the values of  $J$  on p. 422,

$$\begin{aligned} J_1 &= 10547, \quad J_2 = 7275; & \text{hence } J_1 - J_2 &= 3272 \\ [J_1 &= 18985, \quad J_2 = 13095; & \text{hence } J_1 - J_2 &= 5890], \end{aligned}$$

and according to the tabulation on p. 433,

$$\begin{aligned} c_1 &= 0.341, & c_2 &= 0.234, & c_1 - c_2 &= 0.107; \\ h_1 &= 0.000203 & \text{and} & h_2 &= 0.000318 \\ [h_1 &= 0.000113 & \text{and} & h_2 &= 0.000177]; \end{aligned}$$

and

$$\begin{aligned} \rho_2 &= 3272 + 0.107 T_2 - 0.0000575 T_2^2 \\ [\rho_2 &= 5889. + 0.107 T_2 - 0.000032 T_2^2]. \end{aligned}$$

If the combustion takes place without heat supply, then we must substitute  $Q=0$  in equation (63a):

$$\begin{aligned} 3372.63 &= 0.234 T_2 + 0.0001586 T_2^2 \\ [6070.73 &= 0.234 T_2 + 0.00000881 T_2^2], \end{aligned}$$

from which can be determined the temperature at the end of the combustion:

$$\begin{aligned} T_2 &= \left\{ \begin{array}{l} 5409 \\ 3933 \end{array} \right\} \text{ or, according to Celsius, } t_2 = \left\{ \begin{array}{l} 5136 \\ 3660 \end{array} \right\} \\ \left[ T_2 = \left\{ \begin{array}{l} 9736.2 \\ 7079.4 \end{array} \right\} \text{ or, according to Fahrenheit, } t_2 = \left\{ \begin{array}{l} 9276.8 \\ 6220.0 \end{array} \right\} \right]. \end{aligned}$$

The constants for the equation of condition before and after combustion are:

$$\begin{aligned} B_1 &= 70.42 & \text{and} & B_2 &= 46.95 \text{ (Table, p. 421)} \\ [B_1 &= 128.35 & \text{and} & B_2 &= 85.576]. \end{aligned}$$

From

$$p_1 v = B_1 T_1 \quad \text{and} \quad p_2 v = B_2 T_2$$

follows, according to the found temperature values, the pressure ratio

$$\frac{p_2}{p_1} = \left\{ \begin{array}{l} 12.30 \\ 8.95 \end{array} \right\}.$$

From what has been said other examples of the burning of simple combustible gases might easily be adduced; but the calculations are extraordinarily complicated for compound gases, for example with illuminating gas.

If we compare the results of the calculation of the preceding example with the results of the example on p. 426, in which the invariability of the specific heats was assumed, then such considerable differences manifest themselves that we must probably

forbear for the present pursuing the calculations in the indicated way.

In the theory of the combustion process and in the treatment of the experimental results of Mallard and Le Chatelier and of those of Langen it was expressly assumed that the combustible gases, as well as the products of combustion, were subject to the equation of condition  $p v = B T$  of gases and that therefore the specific heat could be regarded as only a function of the temperature. This assumption is certainly not valid for the products of combustion, carbonic acid and the vapor of water, for with these the specific heat must be regarded as a function of the temperature and of the pressure. The most recent investigations are directed to this very problem; so long as this is not satisfactorily solved there exists a very unfortunate gap which renders every further attempt to pursue these questions theoretically very doubtful of success.

Nevertheless progress in gas-engine construction has been perfectly extraordinary in the last few years and is due to the common efforts of many which have called forth numberless separate observations and practical experiences. Systematic experiments on gas engines, which will embrace all the separate problems, are of pressing need; the mechanical engineering laboratories of the technical high schools, which now exist everywhere, are in some places directing their attention to the experimental investigation of the gas engine, in accordance with the demands of the present day, and will probably soon furnish the necessary basis for a more rigorous, theoretical, treatment of the processes occurring in the engines.

The first complete and carefully conducted experiments on gas engines are due to S l a b y (Verhandlungen des Vereins zur Beförderung des Gewerbflusses); in latter years the distinguished experimental investigations of Eugen Meyer have excited well-deserved attention among engineers. The reports of his experiments are found scattered over the last ten years in the "Zeitschrift des Vereins deutscher Ingenieure," and include different combustion motors of recent date.

## B. DIESEL'S HEAT MOTOR.

### § 76. DISCUSSION OF THE MOTOR AND OF THE NEW VIEWS UNDERLYING IT.

In 1893 R. Diesel published an article "Theorie und Konstruktion eines rationellen Wärmemotors," Berlin, 1893, in which he, starting with special thermodynamic studies, developed views concerning the construction and mode of working of combustion motors which deserved the highest consideration.

The article found on one side complete assent, on the other objections were encountered with respect to the possibility and suitability of practical construction, and with respect to certain portions of the theoretical presentation.

In the meantime, with the cooperation of prominent men and firms and with rare persistence and great sacrifices, different constructions were subjected to careful experimental tests, which indubitably showed that an important invention was under consideration. It was to be foreseen that all the proposals contained in Diesel's article could not be completely realized; Diesel's merit is not diminished thereby, nor ought we to underestimate beforehand the constructive possibilities of our highly developed engineering resources to attain the goal set by Diesel.<sup>1</sup>

Fig. 62, p. 402, which refers to a four-cycle Otto gas engine, will be taken as the basis of the fuller discussion of the new motor; but the dead, or compressing, space  $V_1$ , indicated in Fig. 62a, must be considered much smaller relatively to the space  $V_2$  swept through by the piston; we will likewise assume that work is performed in the four-cycle process.

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<sup>1</sup> A lecture by Diesel gives an insight into the gradual development of the motor: "Diesel's rationeller Wärmemotor," Zeitschrift des Vereins deutscher Ingenieure, 1897, Vol. 41, pp. 785 and 817; also Schröter's report on his excellent experiments with a motor (*ibid.*, p. 845). Further: Diesel's "Mitteilungen über den Dieselschen Wärmemotor" in Zeitschrift, 1899, pp. 36 and 128.

The working of the motor is now as follows:

(a) During the first forward stroke of the piston only atmospheric air is sucked in, and during the adiabatic return it is compressed in the actual constructions to from 30 to 50 atmospheres. In the compression space there is now pure atmospheric air of high pressure and of high temperature, which has been produced exclusively in a mechanical way by adiabatic compression, as was assumed in discussing the Carnot cycle. Into this space Diesel introduced the fuel under great excess of pressure and, from the first, thought of utilizing a solid fuel (coal dust), liquid fuel (petroleum, naphtha, alcohol), or gaseous fuel (compressed illuminating gas).

(b) The motor does not, like the gas engine, possess a special ignition device, therefore does not have hot tubes, or flames or apparatus for electrical ignition, for the temperature reached by the air during compression is sufficient to effect the ignition of the fuel. The temperature of ignition has a particular value for each fuel under given conditions, and is lower, the higher the pressure at which ignition is introduced; petroleum behaves particularly well in this respect; in fuels which ignite with difficulty the ignition is promoted by a slight admixture of petroleum.

(c) Combustion begins immediately after ignition; the temperature of combustion is a consequence of the chemical occurrences connected with combustion and depends on the quantity of air present, which Diesel uses in great excess in opposition to the hitherto customary view that in ordinary combustion the air supply should, comparatively speaking, be but a little more than is just needed for complete combustion.

(d) The blowing of the fuel into the compression space filled with dense air occurs during the first part of the return stroke of the piston and occurs gradually, being regulated by the admission nozzle, and thus a certain control is obtained over the course of the curve of combustion to which the expansion curve (adiabatic) then attaches itself.

The starting of the engine is effected by the introduction of

compressed air from a storage reservoir, which is kept filled with compressed air by the motor itself, when running.

We must add that originally the engine worked without a cooling jacket, but that it was added later on with advantage; furthermore, that with a variable load the performance was regulated by varying the supply, i.e., the period of admission of the fuel.

With the first engine built in the engine works at Augsburg, which was specially designed for experimental purposes by Diesel, the very careful and extensive experiments, already mentioned on p. 436, were conducted by Schröter, a fluid fuel, petroleum, being used; for fuller details we must refer to Schröter's report; on account of the importance of the question, we will here adduce at least the principal results.

The petroleum employed had a heating power  $H$  which was on the average  $H = 10206$  cal. [18371 B.t.u.], i.e., this amount of heat was released in the calorimeter when one kilogram [pound] of petroleum was burned completely. This heat quantity is really developed in the cylinder of the engine and can therefore be regarded as the heat quantity available for the performance of work. According to all the general investigations made above it is of course theoretically impossible to produce all the work corresponding to this heat; but if we compare the work actually produced with that just indicated, we get a measure for the excellence of the engine's performance. In so doing there can be taken from the indicator diagrams the indicated work in horse powers ( $N_i$ ), or the effective work ( $N_e$ ) can be obtained with the help of the brake dynamometer and be made the basis of further discussion.

Let  $G_h$  be the weight of the petroleum in kilograms [pounds] which is consumed per hour by the engine, and let  $H$  represent, as before, the heating power, then, according to the usual conception, there will correspond to the available heat quantity a work  $N_0$  in horse powers

$$N_0 = \frac{424}{75 \times 3600} H G_h = 16.027 G_h$$

$$\left[ N_0 = \frac{772.83}{550 \times 3600} H G_h = 7.1704 G_h \right]$$

for the engine investigated; the indicated "efficiency" is then

$$\eta_i = N_i : N_0 \quad \bullet$$

and the effective efficiency is

$$\eta_e = N_e : N_0.$$

The following table gives the most important of Schröter's experimental results (arranged somewhat differently); two sets of experiments (I and II) refer to full load and the other two (III and IV) to half load.

The first three rows give Schröter's observations, the other three rows the results of calculations according to preceding formulas.

	Full Load.		Half Load.	
	I.	II.	III.	IV.
$G_h =$	4.92	4.24	2.66	2.72 kg. (hourly)
$N_i =$	26.56	23.60	16.57	16.52 horse powers
$N_e =$	19.87	17.82	9.58	9.84 " "
$N_0 =$	78.85	67.95	42.63	43.59 " "
$\eta_i =$	0.337	0.347	0.389	0.379 " "
$\eta_e =$	0.252	0.262	0.225	0.226 " "

The efficiencies here attain values which have hitherto never been observed in any other heat motor, and especially deserving of attention are the slight differences they exhibit at different loads.

The consumption of petroleum in kilograms [pounds] per hour, per brake horse power at full load, is in the mean  $G_h : N_e = 0.242$  [0.541], and at half load is 0.276 kg. [0.617 lb.], which are far more favorable values than have been reached by ordinary petroleum motors. More favorable results still than those found by Schröter are said to have been attained in experiments with engines built later. Diesel's motor has probably met the high expectations of the inventor so far as the use of liquid fuels is concerned; as regards the employment of highly compressed illuminating gas and the use of solid fuel in dust form, in place of the liquid fuels, no report has thus far been made concerning the

results of the experiments, but here also success should not be lacking. In the meantime the construction of the ordinary gas motor has progressed, and its improvement is largely to be sought in the use of a high preliminary compression; it has the appearance of having here reached about the limit of improvement of the working process, while with the Diesel motor there seems to be a wider margin in this direction.

Diesel's theoretical preliminary investigations started with the idea of making the cycle of his engine approach as nearly as possible that of the Carnot cycle; Diesel had to give up from the beginning the idea of bringing about a perfect agreement, for, as was already emphasized, this is impossible; on the other hand he sought to follow as closely as possible certain parts of the Carnot cycle. The agreement exists with respect to the expansion and compression curves, but the former is not continued down to the external back pressure, but is broken off earlier, as is moreover the custom with other heat engines, because while the loss of work thus incurred is small, the cylinder dimensions are considerably decreased. The lower curve, isothermal compression at the constant lowest temperature (path *cd*, Fig. 41, p. 285), as in gas engines, is replaced by the initially slightly rising part of the compression curve. As was said before, the compression curve is broken off when the ignition temperature is reached; here begins the introduction of the liquid or gaseous fuel and the regulation of the combustion, in such a way that, so far as possible, it may take place at constant temperature. In this part of the cycle the main difference between the Diesel motor and the gas engine manifests itself to the advantage of the former.

### General Conclusions.

#### § 77. ON THE "WORKING VALUE" OF FUELS.

When considering the closed air engine in § 53, under the head "Disposable Work of Heat Engines" (p. 300), mention was made of the "working value"  $L_0$  of the heat in the heating body and fuller elucidation was reserved. There the efficiency  $\eta = L:L_m$ , where  $L$  is the work actually produced in the engine and  $L_m$  repre-

sents the disposable work, the latter, calculated under the hypothesis that the engine describes the perfect cycle (according to C a r n o t ), is determined by the formula

$$AL_m = \frac{Q_1}{T_1}(T_1 - T_2), \quad . . . . . (1)$$

but in so doing it is expressly assumed that the working or mediating body is supplied with the heat quantity  $Q_1$  from the outside, the heat coming from a special heating plant and passing through walls before entering the medium, and that  $T_1$  and  $T_2$  represent respectively the highest and lowest temperatures occurring in the cycle. Engines of this sort we will here designate as "external-combustion engines"; steam and hot-air engines are of this sort.

In applying the preceding formula the analogy of the heat engine to the hydraulic motor was repeatedly mentioned and made manifest; when the disposable work  $L_m$  is to be determined, the place of the weight or of the "water supply" is taken by the heat weight or the change of entropy  $Q_1:AT_1$  and the place of the "fall" is taken by the temperature difference  $T_1 - T_2$ . In this view the occurrences in the heating plant proper are ignored and so is the heat quantity which is released at the same time by the combustion of the fuel on the grate. If  $B$  is the fuel in kilograms [pounds] per second and  $H$  the heating power, then the heat released is  $BH$ ; it has a very different and indeed a larger value than  $Q_1$  in the last formula, provided that  $Q_1$  and hence  $L_m$  are likewise reduced to the second; neither do the temperatures  $T_1$  and  $T_2$  stand in any direct relation to the combustion temperature in the furnace and to the temperature with which the products of combustion leave the heating surface.

The cost of running a heat engine depends upon the fuel consumed and therefore one is accustomed, in comparing the excellence of different engines, to immediately base the comparison on the fuel which they consume.

If  $L$  is again the work per second performed by the engine, and here we may think of either the indicated work  $L_i$  or of the effective work  $L_e$ , then the heat value is  $AL$ , and its comparison



with the heat quantity  $BH$ , simultaneously generated on the grate, will furnish the measure.

If we substitute

$$\eta_w = \frac{AL}{BH}, \quad . . . . . (2)$$

we can (according to Grashof) designate  $\eta_w$  as the economic efficiency of the engine.

If the work of the engine is given in horse powers and is designated by  $N$ , and if  $B_h$  represents the fuel consumed per hour, then  $L = 75N$  [ $L = 550N$ ] and  $B_h = 3600B$ ; hence we also have

$$\eta_w = 75 \times 3600 \frac{AN}{B_h H} \left[ 550 \times 3600 \frac{AN}{B_h H} \right]. \quad . . . . (2a)$$

Here we can, at pleasure, choose for  $N$  the indicated work  $N_i$  or the effective work  $N_e$ .

If in equation (2) we substitute for  $L$  the value  $L_m$ , according to equation (1), and replace the value  $\eta_w$  by  $\eta_h$ , then for external-combustion engines

$$\eta_h = \frac{AL_m}{BH} \quad . . . . . (3)$$

can be regarded as the "economic efficiency of the heating plant."

The value  $B_h:N$  in equation (2a) means the fuel per hour per horse power; with indicated work we estimate, for the best steam engines of the present day,  $B_h:N_i = 1$  kg. [2.2 lb.] of coal (Steinkohle), and as  $H = 7500$  cal. [13500 B.t.u.] may be assumed for this coal, it follows from equation (2a) that the economic indicated efficiency is  $\eta_w = 0.085$ , and referred to the effective power ( $N_e:N_i = 0.85$  is assumed) we have  $\eta_w = 0.072$ ; therefore the heat utilization in the best steam engines seems to be imperfect to the highest degree; it appears absolutely as a frightful destruction of the precious and constantly diminishing fuel, coal (Steinkohle), furnished us by nature. In this way the best engines have been judged since the time of Redtenbacher. Although no objection can be urged against the preceding propositions from the purely practical stand-

point, so far as it involves a comparison of different engine types with the help of the economic efficiency  $\eta_w$ , based on equation (1), nevertheless it is thoroughly inadmissible to employ  $\eta_w$  offhand in the manner just given, for estimating the excellence of a particular engine, or for judging our best steam engines. In so doing it is tacitly assumed that it is possible to completely transform into mechanical work the heat of combustion  $H$  belonging to 1 kg. [lb.] of fuel. If we designate the corresponding work by  $L_0$ , then this assumption is that

$$AL_0 = H; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

now if we could conduct the perfect cycle (C a r n o t), with the fire gases, and in equation (1) replace  $Q$  by  $H$ , then we should get the preceding relation by supposing  $T_2=0$ , as has already been emphasized. The expansion in the C a r n o t cycle would therefore have to be prolonged till the lowest limit of temperature, the absolute zero, was reached, which is impossible; it resembles charging an hydraulic plant in the interior of the country with a fall that is measured from the level of the head-race to the level of the sea. Therefore if, for a particular type of engine, it is desired to express the efficiency in terms of work which is actually available, we must determine a quantity  $L_0$ , already designated as "working value of the fuel," but which cannot at all be determined according to equation (4) but must be calculated in a special way. The working value  $L_0$  depends on the process of combustion and on the temperature limits between which this process can, in principle, be conducted. The process will be different in the various engine types; it is only necessary to think of the ordinary steam-boiler plant or of the combustion in the gas engine, or in the Diesel motor; in each discussion that combustion process is taken as a base, which actually exists with the engine considered, and in so doing we at the same time consider this process the most profitable for the case under consideration. Of course this does not exclude the possibility of considering some other unknown process of combustion (following some other combustion curve) which will lead to other results.

## (a) External-combustion Engines.

Let us next consider the ordinary steam-boiler plant in which solid fuels are burned under constant atmospheric pressure  $p_0$ .

Let the atmospheric air enter the furnace with the specific volume  $v_0 = OA_0$  and the atmospheric temperature  $T_0$ , and let

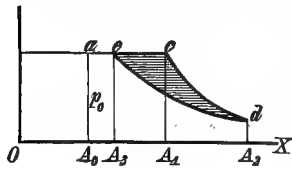


FIG. 64.

combustion begin at the point  $a$  and stop at the point  $c$ . The curve of combustion is therefore represented by the horizontal straight line  $ac$ .

Now from the point  $c$  let the process with the fire gases be continued in the following manner. Let the products of combustion first expand adiabatically according to the curve  $cd$  till it reaches, at the point  $d$ , the lower temperature limit  $T_0$  and then compress these products at the constant lowest temperature  $T_0$  (isothermally with a corresponding withdrawal of heat) till atmospheric pressure  $p_0$  is again reached at the point  $e$ ; in this condition the mass of gas is technically worthless and is now pushed into the open air under the constant pressure  $p_0$  which corresponds to an expenditure of work represented by the rectangular area standing over  $OA_3$  (Fig. 64). It is evident that we have here a closed working cycle before us; the indicator-diagram area, hatched in Fig. 64, gives the work produced in this cycle, and this now represents the working value of the fuel. If the work area  $ecd$  is first reduced to a kilogram [pound] of the fire gases (products of combustion), and if we designate by  $v_1$  and  $v$  the specific volumes belonging to the points  $e$  and  $c$ , and the corresponding temperature values by  $T_0$  and  $T$ , then the work produced along the path  $ec$ , expressed in units of heat, is

$$AL_1 = Ap_0(v - v_0) = AB(T - T_0); \quad . \quad . \quad . \quad (5)$$

here it is always permissible to assume that the gas constants ( $B$ ,  $c_p$ , and  $c_v$ ) are the same for air and for the fire gases;  $T$  is the temperature of combustion.

The work  $L_2$ , performed during adiabatic expansion along the path  $cd$ , is found (equation 62a), p. 140, from equation

$$AL_2 = c_v(T - T_0). \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Finally the work  $L_3$  expended along the path  $de$  is found from isothermal compression, i.e.,

$$AL_3 = ABT_0 \log_e \frac{p_0}{p_2}$$

(equation 58a), p. 138, when the pressure at the point  $d$  is designated by  $p_2$ .

For adiabatic expansion the equation

$$\frac{p_0}{p_2} = \left( \frac{T}{T_0} \right)^{\frac{\kappa}{\kappa-1}}$$

(equation 61, p. 139) holds, and because

$$\frac{\kappa}{\kappa-1} = \frac{c_p}{c_p - c_v} = \frac{c_p}{AB},$$

it follows that

$$AL_3 = c_p T_0 \log_e \frac{T}{T_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The work area  $L_0$ , hatched in Fig. 64, is determined by  $L_0 = L_1 + L_2 - L_3$ , and therefore with the utilization of the preceding formulas,

$$AL_0 = c_p \left[ T - T_0 - T_0 \log_e \frac{T}{T_0} \right],$$

reduced to the unit of weight of the products of combustion.

Let  $G$  be the weight of the products of combustion per kilogram [pound] of fuel, then the working value  $L_0$  of the fuel is

$$AL_0 = c_p G \left[ T - T_0 - T_0 \log_e \frac{T}{T_0} \right]. \quad . \quad . \quad . \quad . \quad (8)$$

The weight of air necessary for combustion here amounts to  $(G-1)$  kg. [lb.].

If, for example, in a particular boiler plant we assume the temperature of the atmospheric air to be  $t_0=20^\circ\text{C}$ . [ $68^\circ\text{F}$ .] and the temperature of combustion in the furnace to be  $t=1200^\circ\text{C}$ . [ $2192^\circ\text{F}$ .], and accordingly  $T_0=293^\circ$  [ $527.4^\circ$ ] and  $T=1473^\circ$  [ $2651.4^\circ$ ], which to be sure already presupposes a certain imperfection of combustion, then for the mean value  $c_p=0.24$ , equation (8) gives

$$AL_0=169.64\ G\ [AL_0=305.35\ G].$$

If we suppose coal (Steinkohle) firing and estimate the quantity of air, per kilogram, of coal to be 16 kg. [lb.], and therefore  $G=17\text{ kg. [lb.]}$ , then for the present case the working value of the coal, measured in units of heat, is

$$AL_0=2884\text{ cal. }[AL_0=5191\text{ B.t.u.}],$$

while its heating value, based on the combustion in the calorimeter is taken up at the mean value  $H=7500\text{ cal. [13,500 B.t.u.]}$ .

The heat  $Q_1$  here released upon the grate is

$$Q_1=c_pG(T-T_0)=4814\text{ cal. [8665.2 B.t.u.]}$$

Hence follows from equation (8)

$$AL_0=Q_1\left[1-\frac{T_0}{T-T_0}\log_e\frac{T}{T_0}\right], \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and with the assumed temperature values

$$AL_0=0.599\ Q_1=2884\text{ cal. [5191 B.t.u.]}$$

as before.

If we now substitute the value  $AL_0$  for  $H$ , in equation (2a), assume the indicated performance  $N_i$  for  $N$ , and designate the efficiency by  $\eta$ , we have

$$\eta=0.221\frac{N_i}{B_h}.$$

If we again estimate for the best steam engine 1 kg. [2.2 lb.] of coal (Steinkohle) per indicated horse power, we get

$$\eta=0.221,$$

which is nearly three times greater than was found on p. 442, even though this value seems still unfavorable enough.

In order to get a greater insight into the conditions, let us emphasize the following. In the here assumed engines (steam or hot-air engines) the fire gases, while flowing along the so-called heating surface, deliver a part of their heat to the mediating body confined in the interior of the engine. Let  $T'$  be the temperature with which the fire gases leave, and flow away from, the heating surface, then the heat quantity  $Q$ , per kg. [lb.] of fuel, which is placed at the disposal of the engine itself, is:

$$Q = c_p G (T - T');$$

and the work  $L_m$ , which is here produced when the engine describes a C a r n o t cycle between the limiting temperatures  $T_1$  and  $T_2$ , is

$$L_m = \frac{Q_1}{AT_1} (T_1 - T_2),$$

or, utilizing the value of  $Q$ ,

$$L_m = \frac{c_p G}{AT_1} (T - T') (T_1 - T_2), \quad . \quad . \quad . \quad (10)$$

which magnitude can be presented as the disposable work of the prime mover.

Now the ratio  $L_m : L_0$  represents the important magnitude  $\eta_h$ , which can be regarded as the efficiency of the heating plant, and in combination with equation (8) it can be determined from

$$\eta_h = \frac{(T - T') (T_1 - T_2)}{T_1 \left[ T - T_0 - T_0 \log_e \frac{T}{T_0} \right]}. \quad . \quad . \quad . \quad (11)$$

In order to again insert a numerical example let the temperatures be  $t = 1200^\circ \text{ C.}$ ,  $t_0 = 20^\circ \text{ C.}$  [ $2192^\circ \text{ F.}$  and  $68^\circ \text{ F.}$ ], and let the temperature at which the fire gases leave the heating surface be  $t' = 300^\circ \text{ C.}$  [ $572^\circ \text{ F.}$ ] and let the C a r n o t cycle be described between the temperatures  $t_1 = 180^\circ \text{ C.}$  [ $356^\circ \text{ F.}$ ] and  $t_2 = 20^\circ \text{ C.}$  [ $68^\circ \text{ F.}$ ]. Equation (11) then gives for the efficiency of the heating plant

$$\eta_h = 0.450.$$

From the smallness of this value it undoubtedly follows that the efficiency, found above for the best steam engines, is not to be charged against the steam engine proper, but is due to the kind of heating and to the steam production in the boiler. That is why in all my earlier publications on steam engines I have rigorously distinguished the efficiency of the engine from the efficiency of the whole plant (inclusive of the heating), as I did above in air engines.

Equation (11) gives rise moreover to an additional remark.

The temperature  $t'$  with which the fire gases leave the heating surface is always greater than the upper temperature limit  $t_1$  of the cycle described by the engine, greater, for example, than the steam temperature in the steam boiler. If we substitute  $t' = t_1 + \tau$  and again  $t_2 = t_0$ , equation (11) gives

$$\eta_h = \frac{(T - T_1 - \tau)(T_1 - T_0)}{T_1 \left[ T - T_0 - T_0 \log_e \frac{T}{T_0} \right]}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (11a)$$

For a particular value of the combustion temperature  $T$ , for the atmospheric temperature  $t_0$ , and for the excess  $\tau$ , this equation gives a most profitable value for the upper temperature limit  $T_1$  or  $t_1$  of the C a r n o t cycle, and thus furnishes a maximum for the efficiency of the heating plant. We get, as is easily seen,

$$T_1 = \sqrt{T_0(T - \tau)}.$$

For  $\tau = 100^\circ \text{ C. } [180^\circ \text{ F.}]$ , for the above-used values  $t = 1200^\circ \text{ C. } [2192^\circ \text{ F.}]$  and  $t_0 = 20^\circ \text{ C. } [68^\circ \text{ F.}]$  we get  $T_1 = 633^\circ [1139^\circ]$ , or  $t_1 = 360^\circ \text{ C. } [680^\circ \text{ F.}]$ , and  $\eta_h = 0.562$  for a maximum.

The temperature value  $t_1$  here found may occur in hot-air engines, but in the earlier discussion of these engines it was stated that this upper temperature limit ought to be chosen as high as possible; now the limitation presents itself, that with these engines a certain upper value should not be exceeded; for while this excess increases the efficiency of the engine, it diminishes that of the heating plant.

The foregoing considerations confirm the view, expressed

long ago, that external-combustion engines, hence such as possess special heating plants, utilize imperfectly in a mechanical way, the heat of the fuel, which fact unfortunately applies to steam engines in which really extraordinary results have been accomplished with the prime mover proper. It seems that no essential betterment of the heating plant itself is to be expected, and that the effort to produce greater and more perfect combustion engines are thoroughly justifiable.<sup>1</sup>

### (b) Internal-combustion Engines.

Let the investigation be again confined to a special case and let the "working value of illuminating gas" be determined for the Otto gas motor. At the beginning of the cycle let there be in the cylinder the volume  $V_0$  of a mixture of illuminating gas and atmospheric air, and let it include a remnant of the products of combustion (Fig. 65a); the pressure  $p_0$  and the temperature  $T_0$  correspond to the values of the external atmosphere. First let the mixture be compressed adiabatically along the path  $T_0T_1$  till the pressure has risen to  $p_1$  and the temperature to  $T_1$ .

Let combustion begin at the point  $T_1$  and let it be concluded at the temperature  $T_2$ ; let the products of combustion expand adiabatically from  $T_2$  to  $T_0$  till the lower temperature limit  $T_0$  is again attained; let the corresponding pressure  $p_2T_0$  be designated by  $p_2$ . Finally let the mass be compressed isothermally till the initial point  $p_0$  is again reached, which will be the case

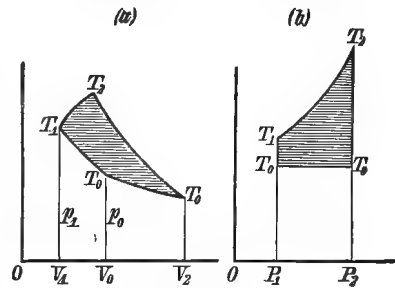


FIG. 65.

<sup>1</sup> The investigation given above, with the derivation of the fundamental equation (11), is already found in the edition of the year 1887. Later Lorenz in the *Zeitschrift deutscher Ingenieure*, 1894, p. 1450, and in 1895, p. 1239, under the title "Die Beurteilung der Dampfkessel," developed the same formulas in a somewhat different way, assuming a cycle presented above as the Lorenz cycle.



when we make what was proved above to be a permissible assumption that the gas constants  $B$ ,  $c_p$ , and  $c_v$  may be taken as equally large for the mixture and for the products of combustion. The area, hatched in Fig. 65*a*, now represents the working value  $AL_0$  of  $G$  kg. [lb.] of the mixture, when  $G$  represents the weight of the mixture consumed per period. Since, in accordance with the hypothesis, the mass has returned to the initial state we can transform the indicator diagram by means of the known propositions. Fig. 65*b* shows the corresponding entropy diagram. Its line  $T_1T_2$  represents the transformation of the curve of combustion, while the area  $P_1T_1T_2P_2$  lying under it is proportional to the heat  $Q$  released during combustion, and at the same is proportional to the produced work  $L$ ; the two values  $Q$  and  $L$  should be reduced to the unit of weight of mixture.

The hatched area in the entropy diagram gives the working value  $AL_0$  measured in units of heat; therefore we at once have

$$AL_0 = G[Q - AT_0(P_2 - P_1)]. \quad . \quad . \quad . \quad (12)$$

Now, in order to include an infinite number of special cases and all technically important ones, we will assume a curve of combustion to be a polytropic curve having the course  $pv^n = \text{constant}$ , of which the corresponding specific heat  $c$  is given by (p. 152)

$$c = \frac{n - \kappa}{n - 1} c_v,$$

then  $dQ = cdT$  and  $AdP = c \frac{dT}{T}$ , and there follows at once from equation 12

$$AL_0 = cG \left[ T_2 - T_1 - T_0 \log_e \frac{T_2}{T_1} \right], \quad . \quad . \quad . \quad (13)$$

because

$$Q = c(T_2 - T_1). \quad . \quad . \quad . \quad (14)$$

The work  $L$  produced during combustion is given by equation (7) (p. 153):

$$AL = (c - c_v)(T_2 - T_1). \quad . \quad . \quad . \quad (15)$$

If the compression relation is  $p_1:p_0$ , we can get the temperature at the end of compression from

$$\frac{T_1}{T_0} = \left( \frac{p_1}{p_0} \right)^{\frac{\kappa-1}{\kappa}} \cdot \cdot \cdot \cdot \cdot \cdot \quad (16)$$

If we refer the weight  $G$  of the mixture to one kilogram (pound) of illuminating gas, equation (13) will at once give the working value  $L_0$  per kilogram (pound) of gas.

If there were no compression, then we should have  $p_1=p_0$ , and should have to make  $T_1=T_0$ .

In equations (14) and (15) the values  $Q$  and  $L$  refer to 1 kg. [lb.] of mixture; with  $G$  kg. [lb.] of mixture we must therefore write

$$Q = cG(T_2 - T_1), \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (14a)$$

where  $Q$  refers to  $G$  kg. [lb.] of illuminating gas.

Unfortunately the experiments known at the present time do not render it possible to utilize the preceding formulas with any degree of certainty. If we assume, as seems permissible for many cases, combustion at constant volume, we must substitute specific volume  $c_v$  at constant volume in place of  $c$ . The uncertainty indicated lies in our ignorance of the combustion temperature  $T_2$ , and hence, according to equation (14a), the heat quantity  $Q$  released during combustion cannot be determined; the basis for these problems will only be furnished by experiments which may be expected in the future.

In order, however, to get an insight with the help of an example let us assume  $c=c_v$ ; then follows

$$AL_0 = c_v G \left( T_2 - T_1 - T_0 \log_e \frac{T_2}{T_1} \right) \cdot \cdot \cdot \cdot \cdot \quad (13a)$$

If it is assumed that the combustion was perfect, we must put in place of  $Q$  in equation (14a) the heating power  $H$  of illuminating gas, where  $G$  is the weight of the mixture for 1 kg. [lb.] of illuminating gas; then

$$H = c_v G (T_2 - T_1) \cdot \cdot \cdot \cdot \cdot \quad (14b)$$

Here the influence of the cooling of the cylinder walls should certainly find expression, for this action prescribes a smaller value for the combustion temperature  $T_2$ .

If there is preliminary compression,  $T_1$  can be computed from equation (16), and by the known value of  $G$  the temperature  $T_2$  can be found, and finally the working value  $L_0$ , according to equation (13a).

**Example.** For the illuminating gas of average composition (p. 412), there is found  $H=10113$  cal. [18203 B.t.u.].

For this illuminating gas there was found  $B=60.823$  [ $B=110.86$ ], and for a mixture of gas of the proportions 19 kg. [lb.] of air to 1 kg. [lb.] of gas, i.e., for  $G=20$  kg. [lb.] there was found  $c_v=0.1837$  and  $B=30.846$  [ $B=56.223$ ].

Let the initial temperature be  $t_0=20^\circ$  ( $68^\circ$  F.),  $T_0=293^\circ$  [ $527.4^\circ$ ], and before ignition suppose the mixture of one atmosphere pressure to be compressed up to three atmospheres, then according to equation (16) there is determined  $T_1=403^\circ$  [ $725.4^\circ$ ], and, from equation (14b),

$$T_2 = \frac{H}{c_v G} + T_1 = 3156^\circ$$

$$\left[ T_2 = \frac{H}{c_v G} + T_1 = 5681^\circ \right];$$

accordingly  $t_2=2883^\circ$  [ $5221.4^\circ$ ], a very high value at which dissociation occurs; to be sure, as was mentioned, the cooling influence of the cylinder walls was completely neglected. From equation (13a) there can now be determined, for the assumed illuminating gas, the "working value" measured in heat units:

$$AL_0 = 7898 \text{ cal. [14216 B.t.u.]}$$

From the equation of condition  $p_0 v = BT_0$ , for the atmospheric pressure  $p_0=10333$  [2116.3], and for the temperature  $t_0=20^\circ$  C. [ $68^\circ$  F.] we find, for the illuminating gas (with the given value of  $B$ ), the specific volume  $v=1.4727$  [23.591] and, for atmospheric air at the same pressure and at the same temperature,  $v=0.8299$  [13.294]; as 19 kg. [lb.] of air are mixed with 1 kg. [lb.] of gas, the air volume  $V$  is  $19 \times 0.8299 = 15.7681$  cbm. [252.59 cu. ft.], according to which we must count on 9.14 cbm. [cu. ft.] of air for every 1 cbm. [cu. ft.] of gas.

That the working value of 1 kg. [lb.] of illuminating gas is considerably greater than that found on the average for 1 kg. [lb.] of coal (Steinkohle) is explicable if we would compare fuel con-

version in the gas engine with that in the steam engine. We ought really to introduce into the calculation the quantity of coal needed for the generation of the illuminating gas.

If, in the example calculated on p. 446, we take the working value of the coal to be 2884 cal. [5191 B.t.u.], and, on the other hand, according to the preceding example, the working value of the illuminating gas to be 7898 cal. [14216 B.t.u.], then the latter value is 2.74 times the former; as, in the best steam engines, we can count on an hourly consumption of 1 kg. [lb.] of coal [Steinhohle] per indicated horse power, then, in a gas engine of equal excellence, we could count on an hourly consumption of 0.365 kg. [0.8 lb.] or 0.63 cbm. [22.25 cu. ft.] per indicated horse power, a value which is, in fact, nearly approached in good gas motors; accordingly these engines are to be placed equal to the best steam engines—a result which, for the present, we must accept with caution, for the preceding calculations are still loaded with uncertainties because of the indefiniteness of several of the assumed values.

Diesel's motor, like Otto's, might have been subjected to the same line of investigation, but we have avoided doing so because here similar indefiniteness would arise. For the purpose of testing the preceding propositions it is necessary that the illuminating gas used in the engine considered should be exactly examined beforehand as to its physical properties, namely, as to the gas constants  $B$ ,  $c_p$ , and  $c_v$ , and also as to its heating power  $H$ , and that ways and means be found to determine the combustion temperature  $T_2$  in the engine itself. From the observed indicated and effective work  $L_i$  and  $L_e$ , with the help of the computed working value  $L_0$ , can be determined the corresponding efficiencies; consequently there still exist here plenty of problems for experimental investigation.



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